Concern for man and his fate must form the chief interest of all technical endeavors. Never forget this in the midst of your diagrams and equations

- Albert Einstein

I have named the destroyers of nations: comfort, plenty, and security – out of which grow a bored and slothful cynicism, in which rebellion against the world as it is, and myself as I am, are submerged in listless self-satisfaction

- John Steinbeck

To possess uniqueness is useless without first having someone to share it with and, secondly, having the ability to appreciate it in others.

- Matthew Good

University of Alberta

Trophodynamics of Organochlorine Pesticides in the Aquatic Food Web of Lac La Biche, AB

by

Derek Scott Bleackley ©

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Abstract

The determination of concentrations and enantiomeric fractions of both chiral and achiral OCPs in the Lac La Biche aquatic food web were carried to elucidate sources, bioaccumulation, and tropodynamics of target compounds. Organochlorine pesticides were detected in the Lac La Biche food web and biomagnification is occurring. γ-HCH is a major pollutant in the fishes of Lac La Biche. Adult cormorants appear to have sufficient biological capacity to eliminate γ-HCH and appear to contain completely different organochlorine pollutants compared to other organisms of the food web. Cormorants exhibit particularly high EFs for oxychlordane and heptachlor-*exo*-epoxide. Double-crested cormorants appear to be a means of removal for local-source pollutants from Lac La Biche; however, more recalcitrant pollutants from other locales are brought to Lac La Biche by these same birds. Northern pike appear to enantioselectively compartmentalize α-HCH in different tissues.

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1 Background Information

The following chapter covers the some of the background literature relevant to appreciate the content, scope and overall goal of this thesis. Covered in Chapter One are topics such as: chirality and its significance in the environment, bioaccumulation, stable isotope analysis, target compound history and toxicity information.

Chapter Two contains experimental methods, results and discussion. Experimental methods include: sample retrieval and handling, extraction, clean-up, instrument parameters, quality control, and statistical methods employed. Results are presented in four subsections: forage fishes, piscivorous fishes, double-crested cormorants, and double-crested cormorant eggs. Comparison of determined and literature concentrations are also included in the preceding sections. The foci of the Discussion section are occurrence and fate of the target compounds throughout the overall food web, with emphasis on enantiomeric fractions.

The third chapter covers future directions for the work initiated herein, as well as the study of enantioselective trophodynamics in general.

1.1 Chirality

Chirality arises from the ability of molecules to be non-superimposable mirror images, called enantiomers. For a molecule to be chiral it must posses an asymmetric feature such as a point, an axis, or a plane. A point of asymmetry is created when an sp^3

hybridized atom has four different substituents attached (Figure 1.1). Such an atom is referred to as a chiral centre.

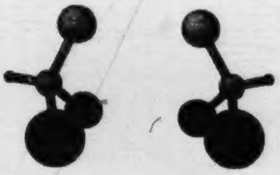


Figure 1.1: An enantiomer pair of *sp*^{3} hybridized atoms with four different substituents.

An axis of asymmetry occurs in molecules where the energy barrier to rotate a bond is higher than that encountered under environmental conditions. A high-energy requirement for rotation occurs when large substituents prevent the free rotation about an asymmetrically substituted bond, such is the case with 2,2',3,5',6-pentachlorobiphenyl (PCB 95) (Figure 1.2).

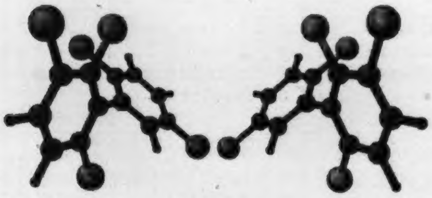


Figure 1.2: Hindered rotation of PCB-95, due to asymmetric chlorine substitution about the phenyl bond.

Bond rotation is completely prevented in some molecules that contain either a ring structure, a double bond or an atropisomeric bond. An atropisomeric bond has hindered rotation at temperatures encountered in the environment, and compounds with these bonds may be found as enantiomers. The pesticide metolachlor possesses two atropisomeric bonds (phenyl-N and N-CO) and an asymmetrically substituted carbon (Figure 1.3) (Aga *et al.* 1999). Molecules having hindered rotation caused by double bonds or cyclic structures are generally labeled based on relative stereochemistry. The relative stereochemistry of molecules is given as either *cis*- or *trans*-, based of where the priority groups lie with respect to one another (Figure 1.4).

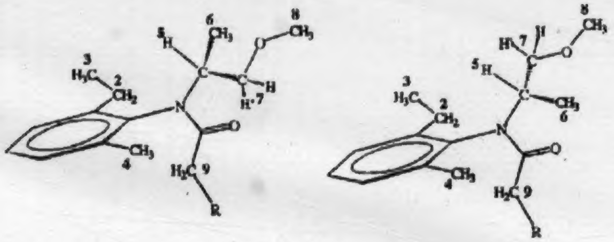
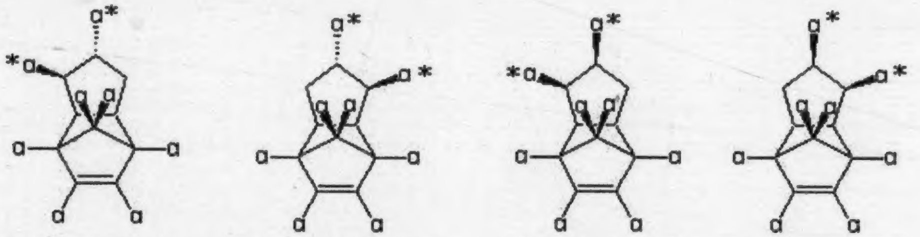


Figure 1.3: Conformations of metolachlor.
left: s-*trans*,aR,5R and right: s-*trans*,aR,5S Reprinted with permission from (Aga *et al.* 1999). Copyright (1999) American Chemical Society

Cis- molecules have both groups on the same side of the double bond or above the ring, whilst *trans*- molecules have priority groups on opposite sides of the double bond or above and below the ring. Planar asymmetry generally occurs when closed rings are asymmetrically substituted, as is the case with *cis*- and *trans*- chlordane (Figure 1.4)



(+)-*trans*-chlordane (-)-*trans*-chlordane (+)-*cis*-chlordane (-)-*cis*-chlordane

Figure 1.4: *trans*- and *cis*- chlordane.
Notice the position of the chlorine substituents denoted by asterisks.

Enantiomers have identical physical and chemical properties. One method of differentiating between enantiomers is based on the direction that plane polarized light is rotated. When viewing the beam of light, looking towards the source, clockwise rotation is denoted as dextrorotatory or (+), and counterclockwise rotation is labeled as levorotatory or (-). Note that *R*-, *S*- designation cannot be used to determine the direction that plane polarized light will rotate (Buser *et al.* 1995a). The rotation amount of plane-polarized light is dependent upon factors such as path length, temperature, concentration, purity and the wavelength of light. A second method used for differentiating between enantiomers utilizes chiral chromatography of either an enantiomerically pure standard or one with a known enantiomer enrichment. The absolute stereochemistry of a chiral centre cannot be determined by chiroptical methods. Nuclear magnetic resonance (NMR) methods have been used to determine enantiomeric purity. These methods include the use of chiral derivatizing agents, chiral lanthanide shift reagents, or chiral solvating agents (Parker 1991). Compounds having hindered rotation are often labeled differently see Figure 1.3.

1.1.1 Chiral Chromatography

The application and commercial availability of chiral selectors (CSs) to various separation methods, such as gas and liquid chromatography and capillary electrophoresis, has made it possible to resolve compounds into separate enantiomers. Despite the utility of liquid chromatography and capillary electrophoresis for the separation of chiral compounds, only gas chromatography will be discussed.

Chiral gas chromatography (chiral GC) was developed by Gil-Av *et al.* (1966). Three distinct types of chiral stationary phases (CSPs) have been investigated for use with GC analysis. The three CSPs are distinguished based on their mode of chiral interaction.

The three modes are hydrogen bonding (amino acid derivatives), coordination (metal complexes) or inclusion (cyclodextrins). The CSPs used for the separation of organochlorine enantiomers generally rely on CSs composed of cyclodextrins (CDs).

Cyclodextrins used for chiral GC are composed of six or more D-(+)-glucose units bonded through α-(1,4)-glycosidic linkages (Jennings *et al.* 1997). The resulting torus-shaped cyclodextrins are hypothesized to interact with enantiomers based on inclusion. However, more factors may play a role in the retention and subsequent elution order of enantiomers, such as hydrogen bonding, dipole-dipole, electrostatic interactions, dispersion forces, and hydrophobic interactions (Schurig 2001). Many CSPs used in GC are composed of CDs in polysiloxane stationary phases. The concentration of chiral selector in the stationary phase tends to be dilute, as separation efficiency does not increase linearly with increasing CS concentration. The maximum enantioselective separation is reached when the weight percentage of CSs in the stationary phase is 30% for permethylated β-cyclodextins or 50% for derivatives with high molecular mass (Schurig 2001). The ability to separate enantiomers required the development of a standard expression to represent the difference in the amount of the each enantiomer present: enantiomeric ratios (ERs), enantiomeric fractions (EFs), and enantiomeric excesses (ee). Each of these aforementioned expressions have benefits as well as drawbacks to their usage, and will each be considered separately.

1.1.1.1 Enantiomeric Ratio

Enantiomeric ratio is defined as E_1/E_2, where E_1 and E_2 are the first and second eluting enantiomers respectively. For compounds with a known elution order the ER is expressed as (+)/(-). There are problems with using ER as a method to convey enantiomeric information (Ulrich *et al.* 2003). First, the data has no minimum or maximum limit and becomes undefined when only one enantiomer is present. Second, data is skewed making any error expression dependent on the direction in which it occurs, see section 1.1.1.2. To alleviate these problems, most scientists in the environmental field have adopted the use of the enantiomeric fraction.

1.1.1.2 Enantiomeric Fraction

Enantiomeric Fraction (EF) is a useful method to express chiral signatures (Harner et al., 20002; de Geus et al., 2000). EF is expressed as $E_1/(E_1+E_2)$, where E_1 and E_2 are the first and second eluting enantiomers respectively. If the elution order is known, (+)/((+)+(-)) is used to express the EF. A racemic mixture has equal proportions of both enantiomers, and therefore an EF of 0.5. It is advantageous to use EF because unlike ER, it is bound from 0 to 1 and regardless of the EF value the error associated is independent of the direction in which it occurs as the scale is additive (Ulrich *et al.* 2003).

Assume the hypothetical peak areas of a pair of enantiomers are 120 and 200, respectively. The resulting ER is 0.60, and the EF is 0.37. After further experimentation it is determined that the (-)- enantiomer elutes first. The resulting ER and EF are 1.7 and 0.63, respectively. A value of 0.500 results from computing the mean of the EFs, whilst the mean of the ERs is 1.13, not 1.00 as would be expected. This is an example of how larger ERs are favoured over smaller ERs. Consequently, errors associated with ERs greater than 0.5 are disproportionately large as well. If the uncertainty in the determination of the areas above is ±5, the standard deviation of the resulting ERs would be 0.03 or 0.09 for ERs of 0.06 and 1.7 respectively. The standard deviation of the EF under the same conditions would be 0.01 independent of the EF value. Although EF has distinct advantages when compared to ER its use must be carefully considered when reporting mean and standard error of data near the boundary limits.

The values near the boundary limits of the EF scale are difficult to determine. The inability to determine the EF accurately is due to one enantiomer's peak being below the detection limit. If this peak is not detected and subsequently recorded as an area of 0 the EF will be moved to 0 or 1. A proposed solution to this is to use the area of a peak at or near the detection limit in lieu of an absent peak (Harner *et al.* 2000).

1.1.1.3 Enantiomeric Excess

Enantiomeric excess (ee) is another method used to express enantiomer concentrations relative to each other. Generally used in the drug discovery and synthetic fields, it is expressed as: 100 × ($C_H - C_L / C_H + C_L$), where C_H and C_L are the enantiomers with the higher and lower concentrations, respectively. A racemate will give an ee of 0, whilst the ee of a pure enantiomer will be unity (Ali *et al.* 2004).

1.2 Why is Chirality Significant?

The biological world is a chiral world. DNA has three different helical forms A-, B-, and Z- all of which are chiral (Bruice 1998). Out of the 20 common amino acids used to create every functioning biological system, 19 are chiral. Given the frequency which chirality occurs it is not difficult to envision enantiomers having unique effects upon any number of biological systems and vice versa.

Monitoring enantiomers of chiral legacy organochlorine insecticides (OCs) is important for a number of reasons. Organochlorines are remarkably resistant to degradation and are ubiquitous throughout the environment as will be illustrated in subsequent sections. Despite the recalcitrant nature of OCs, deviations from a racemic enantiomeric signature (ER, EF or ee) have been detected in the environment (Ulrich *et al.* 1998; Wiberg *et al.* 1998; Wiberg *et al.* 2000; Bidleman *et al.* 2002; Wong *et al.* 2002a; Law *et al.* 2004; Wong *et al.* 2004; Kurt-Karakus *et al.* 2005; Seemamahannop *et al.* 2005). Any deviation in the enantiomeric signature of a chemical is the result of any number of biological processes. Monitoring changing EFs throughout an aquatic food web is significant because it can yield information about accumulation and elimination from aquatic organisms. This information may then be used to create better models of fate processes in the environment or can be applied to remediation or toxicology studies.

1.2.1 Accumulation and Elimination

Chiral molecules have identical physical and chemical properties; so only in a chiral biological system do enantiomers begin to have divergent effects. Accumulation of these compounds is one area where many factors such as sex and tissue composition affect enantioselectivity. Karlsson *et al.* (2000) detected dissimilar enantiomeric signatures of *cis*- and *trans*-chlordane in Atlantic cod (*Gadus morhua*) based upon sex. Male cod had increased levels of the (+)-enantiomers whilst females had increased levels of the (-)-enantiomers. In a study on chiral PCBs in the bowhead whale (*Balaena mysticetus*), Hoekstra *et al.* (2002) determined that male whale had an inverse relationship between PCB-91 concentration and EF, while females did not. Tissues may also either preferentially accumulate or eliminate enantiomers. Ulrich *et al.* (2001) found that rats dosed with α-HCH had ERs greater than unity in the brain. Enantioselective metabolism of α-HCH by the brain was not attributed as the cause of the observed ER increases, as the ERs between low and high temperature incubations were equivalent.

Enantioselective degradation of chiral compounds by microbes has been observed. Examples are numerous and varied depending upon the microbe and the environmental compartment. Law *et al.* (2004) detected preferential degradation of (-)-α-HCH detected compared to the (+)-enantiomer in groundwater at a former pesticide handling facility in Florida. Falconer *et al.* (1997) observed the same enantiomeric signature in soil and muck from farms in the Fraser Valley, BC. In contrast, Buser *et al.* (1995b) found preferential degradation of (+)-α-HCH in sewage sludge.

1.2.2 Toxicity

Toxicity is another property that has received interest with respect to enantiomer specificity. Differing enantiomer toxicities have been observed for various chiral compounds in numerous studies. Miyazaki *et al* (1978) first demonstrated an increased toxicity of (+)-heptachlor *exo*-epoxide in male cockroaches, over that of (-)-heptachlor *exo*-epoxide. Although the difference was slight, approximately 2.3 times greater, further studies of cyclodienes demonstrated the reliance of toxicity on specific absolute stereochemistry. An example of this reliance is the similarity between the structures of (+)-heptachlor *exo*-epoxide and (+)-heptachlor, consequently both enantiomers are more toxic than their corresponding antipodes (Miyazaki *et al.* 1980). Another example of dissimilar enantiomeric activity is that of *o,p'*-DDT enantiomers to human estrogen receptors (Hoekstra *et al.* 2001). The estrogenic activity associated with *o,p'*-DDT was found to be due to the (-)-*o,p'*-DDT enantiomer, in agreement with earlier work using rats (McBlain *et al.* 1976; McBlain 1987a). Obviously chirality and the fate of enantiomers in the environment are of great importance.

Historically OC insecticides have been applied as racemic-technical mixtures. Technical mixtures contain numerous isomers or related chemical components in varying or unknown proportions. Often only one isomer, or one enantiomer, within the technical mixture is required to achieve the desired insecticidal effect. Technical mixture use has meant that large applications have been required to achieve desired effects. The large input of technical mixtures meant that many chemicals were unnecessarily entering the environment, and becoming environmental ballast. Both ballast chemicals and active ingredients may bioaccumulate in the environment.

1.2.3 Chiral Analysis for Source Apportionment

Enantiomeric signatures are not altered by poor analytical recoveries or abiotic processes such as photolysis, hydrolysis, or atmospheric deposition (Bidleman *et al.* 1999). This feature makes chiral analysis a useful technique for source apportionment. Sources of chiral compounds of differing enantiomeric signature when combined will yield a composite enantiomeric signature that may be used to determine the greater input Harner *et al.* (2000):

$$f_1 = \frac{(EF_{mix} - EF_2)}{(EF_1 - EF_2)}$$

Equation 1.1: Source Apportionment.
f_1 = fractional contribution of source 1, EF_{mix} = EF of mixture, EF_1 = EF of source 1, EF_2 = EF of source 2 (Harner *et al.* 2000).

In a separate study, Bidleman (2007) measured decreasing α-HCH concentrations in arctic waters as sampling proceeded east to west. Accompanying this decrease in concentration was an increase in EF, despite observation of degradation of the (+)-enantiomer. It was hypothesized that another input of lower concentration and higher EF may have entered the system in previous years (Bidleman *et al.* 2007). Although the presented example does not definitively state the cause of the observed data, a separate source of α-HCH to the arctic would not have been immediately proposed without monitoring the EF of α-HCH.

1.3 Bioaccumulation

Bioaccumulation is the term used to describe how organisms acquire and store contaminants, such as OCs, encountered in the environmental compartment. Two main processes contribute to the overall accumulation of OCs by organisms. These processes are bioconcentration and biomagnification.

1.3.1 Bioconcentration

Bioconcentration occurs when an organism achieves a higher body burden of a pollutant than that present in the surrounding environment via respiration or surface contact with the contaminated matrix (Gobas *et al.* 1993). Bioconcentration occurs strictly due to the establishment of equilibrium between the organism and the environmental compartment (Gobas *et al.* 1993). Bioconcentration is often expressed as the ratio of the organism concentration to that of the environment.

1.3.2 Biomagnification

Biomagnification is the generally the most significant route of contaminant exposure to aquatic species. Biomagnification is the process that enables organisms to obtain higher contaminant concentrations over those concentrations present in the diet (Gobas *et al.* 1999). One hypothesized model of biomagnification is that based on fugacity (Gobas *et al.* 1993; Gobas *et al.* 1999). The fugacity model states that the uptake of contaminants from the diet is due to an increase in fugacity in the gastrointestinal tract (GIT). Since this model is not an equilibrium process, it is a plausible explanation for the increase in body burden of OCs observed throughout food webs.

1.3.3 Fugacity Model

The fugacity model challenges the idea that uptake is strictly an equilibrium process between the organism and the contents of the gastrointestinal tract. If equilibrium were the only process affecting the uptake of contaminants, by definition, there would be no elevated concentrations observed at higher trophic levels. Fugacity (f) defined in terms of concentration (c) and fugacity capacity (z) is presented in Equation 1.2.

$$c = f \times z$$

Equation 1.2: Relation of concentration to fugacity and fugacity capacity

Using this relationship between fugacity and concentration, it is possible to propose how biomagnification may work. The explanation of fugacity given here is by no means exhaustive. For detailed discussions on fugacity and related equations see Clark *et al* (1990), Gobas *et al* (1999), Mackay (2004), Arnot *et al* (2004). As described by Gobas *et al* (1993) (Figure 1.5), the GIT is assumed to be a well-mixed compartment that receives a constant in flow of food per day (G_D) and emits a constant flow of fecal matter (G_F). When prey is consumed by a predator, it has a specific contaminant concentration C_D defined by Equation 1.2 ($C_D = f_D\ z_D$). If $f_D = f_W = f_G = 1$ then no fugacity increase occurs in the GIT (Figure 1.5a) and there is no net uptake of compound A. When food is absorbed there is initially no uptake of contaminant from the GIT, since $f_B = f_G$. As the absorbed food is replaced by more of the contaminated diet the number of moles of contaminant in the GIT increase, while the volume of the GIT remains constant. The result is an increase in chemical concentration and fugacity, f_G, in the GIT (Figure 1.5b). Digestion of the diet, especially lipids, reduces the fugacity capacity of the GIT (Z_G) below that of the diet (Z_D). The decrease in fugacity capacity of the GIT (Z_G) increases the GIT fugacity (f_G) above that of both the diet (f_D) and the body (f_B) (Figure 1.5c) and there is uptake from the GIT.

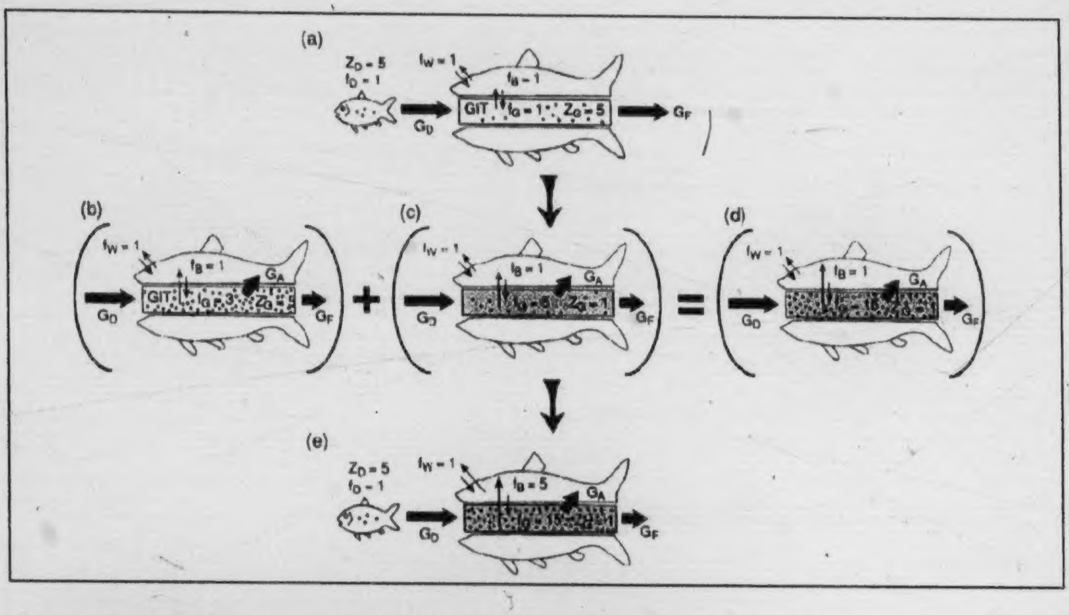

(a)
$Z_D = 5$
$f_D = 1$
$f_W = 1$
$f_B = 1$
GIT
$f_G = 1$
$Z_G = 5$
G_D
G_F
(b)
$f_W = 1$
$f_B = 1$
GIT
$f_G = 3$
G_A
G_D
G_F
+
(c)
$f_W = 1$
$f_B = 1$
$f_G = 5$
$Z_G = 1$
G_A
G_D
G_F
=
(d)
$f_W = 1$
$f_B = 1$
$f_G = 15$
G_A
G_D
G_F
(e)
$Z_D = 5$
$f_D = 1$
$f_W = 1$
$f_B = 5$
$f_G = 15$
G_A
G_D
G_F

Figure 1.5: Diagram of proposed mechanism of biomagnification in fish. terms include in figure defined in text. Reprinted with permission from (Gobas *et al.* 1993). Copyright (1993) American Chemical Society

The uptake of contaminants from the GIT depends upon various factors such as rates of elimination from gills, excretion, metabolic transformation, and growth dilution. Often, the biomagnification factor is used as a method to quantify trophic uptake of contaminants.

1.3.4 Biomagnification factor

A biomagnification factor (BMF), in its simplest form is a ratio expressing the contaminant concentration in the consumer over that of the diet. The BMF has also been proposed as the ratio of body fugacity to diet fugacity (deBruyn *et al.* 2006). The rates of elimination and uptake are affected by the physicochemical properties of the contaminant towards the particular species. The most significant value in the determination of BMF is the octanol-water partition coefficient, or log K_{ow} (Equation 1.3). Buckman et al. (2006)

reported a curvilinear relationship between log $t_{1/2}$ and log K_{ow} for organochlorine contaminants in juvenile rainbow trout (Figure 1.6). Log $t_{1/2}$ is approximately proportional to the BMF.

$$\log K_{ow} = \log \frac{C_o}{C_w}$$

Equation 1.3: Log K_{ow}.
C_o and C_w represent the concentration of compound in immiscible octanol and water phases. Log K_{ow} is used to approximate a compound's affinity for lipids.

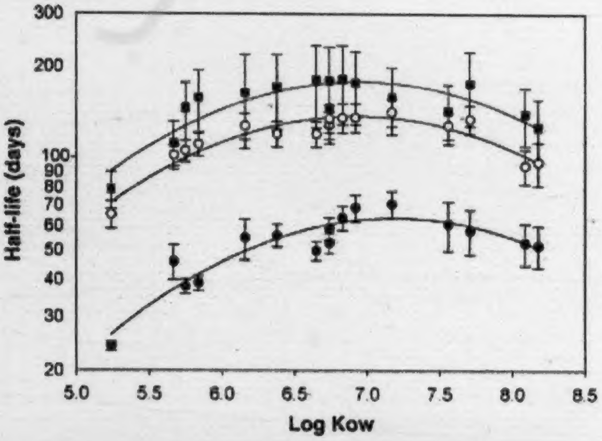


Figure 1.6: Curvlinear relationship between log $t_{1/2}$ and log K_{ow} of 16 recalcitrant PCB congeners in juvenile rainbow trout. Reprinted from Aquatic Toxicology, 78, Buckman et al., Biotransformation of polychlorinated biphenyls (PCBs) and bioformation of hydroxylated PCBs in fish, 176-185, Copyright (2006), with permission from Elsevier.

The log $t_{1/2}$ maximum illustrates that the most readily accumulated contaminants possess log K_{ow}s of approximately 7. Biomagnification of contaminants of K_{ow} greater than 6.3 has also been observed (Russell *et al.* 1999) It is hypothesized that the increase in log BMF for contaminants over the range log K_{ow} 5 to 7 is due to intake being constant while elimination is retarded (Fisk *et al.* 1998). For this reason, biomagnification of compounds with log K_{ow}s less than 6 (Gobas *et al.* 1993) or 5.5 (Russell *et al.* 1999) does not appear to be significant in aquatic food webs, however this is a contentious cut-off point. The decrease of log BMF with respect to increasing log K_{ow} for values greater than 7, is attributed to decreased bioavailability (Bruggeman; Gobas *et al.*) and decreased transport of superhydrophobic contaminants from compartments, such as sediment, to the water column where they become bioavailable (Opperhulzen *et al.* 1985).

1.4 Stable Isotope Analysis

To determine BMFs, it is necessary to determine the trophic positions of the organisms in question in an ecological system. Stable isotope analysis (SIA) is such a technique. The basis of SIA is to measure the abundance of isotopes of elemental nitrogen ($^{15}N/^{14}N$) for trophic level and carbon ($^{13}C/^{12}C$) for trophic position. These ratios are then compared to standard references, Pee Dee belemnite for carbon and atmospheric nitrogen for N_2. Isotopic composition of the material is then obtained by using Equation 1.4 (Peterson *et al.* 1987):

$$\delta X = \left[\left(\frac{R_{Sample}}{R_{Std}}\right) - 1\right] \times 10^3$$

Equation 1.4: Stable Isotope Ratio.
X: ^{13}C or ^{15}N, R: $^{13}C/^{12}C$ or $^{15}N/^{14}N$ (Peterson *et al.* 1987).

Using stable isotopes to establish trophic level relies on the assumption that the composition of the organism's tissue reflects the composition of the bulk diet. This assumption is rarely met as animals metabolize nutrients with different efficiencies (Gannes *et al.* 1997). In a study of avians reared in captivity, the isotopic composition of tissue varied from that of the isotopically homogeneous diet (Hobson 1995). Isotopic routing may also occur, whereby high isotopes are preferentially incorporated into certain tissues; and nutrient allocation is directed to the construction of specific tissues as a means of conserving energy. Isotopic routing is generally only an issue if dissimilar tissues are compared. It has been shown that with consideration of the macronutrient source and proportion present in both the diet and the consumer, the δ values are within 1‰ for similar biochemical components (Schoeller *et al.* 1986). Therefore it is possible to utilize SIA to determine the trophic position of food web components. The apportionment of different isotopes of carbon and nitrogen, which makes SIA a useful technique, relies on the Kinetic Isotope Effect.

1.4.1 Kinetic Isotope Effect

Enrichment of isotopes in organisms is a result of the Kinetic Isotope Effect (KIE). The KIE, a mass dependant effect, is expressed as the ratio of reaction rates of the lighter isotope over that of the heavier isotope. The greater the relative change in mass between the isotopes, the greater the KIE. This means that a compound with a heavier isotope adjacent to the reaction site will proceed at a slower rate than the same compound with a lighter isotope (Elsner *et al.* 2005). The KIE of $^{12}C/^{13}C$ and $^{15}N/^{14}N$ is approximately 1.04 (Laidler *et al.* 2003). In biological systems this effect is more pronounced since isotopic routing may also occur, whereby high isotopes are preferentially incorporated into certain tissues.

1.4.2 Trophic Position

Historically, trophic level determinations have been made by field observation and gut content analysis. Broad terms such as "producer" and "consumer" were used to define the various predator-prey interactions. Attempts have been made to discretely define trophic position based on isotopic signatures. Generally, the trophic level of an organism is defined in terms of $\delta^{15}N$ according to Equation 1.5 (Vander Zanden *et al.* 2001):

$$Trophic\ Level_{Consumer} = \frac{\left(\delta^{15}N_{consumer} - \delta^{15}N_{baseline}\right)}{3.4} + 2$$

Equation 1.5: Trophic Level Calculation.
$\delta^{15}N$: Stable isotope ratio of nitrogen as defined in Equation 1.4.

It is assumed that, due to trophic fractionation, the $\delta^{15}N$ of a predator will be enriched by 3.4‰ over that of the prey (Minagawa *et al.* 1984). This value is based on a single predator prey interaction and, strictly speaking, is not valid for many interactions over multiple levels of the food web (Vander Zanden *et al.* 2001). Additionally, $\delta^{15}N$ has been shown to increase with weight (Rau *et al.* 1981), furthering the difficulty in quantizing trophic level.

1.5 Hexachlorocyclohexane

Hexachlorocyclohexanes (HCHs) are a group of isomers based upon a cyclohexane backbone (Figure 1.7) with the empirical formula $C_6H_6Cl_6$. HCHs are often identified by the position of the substituent chlorines as being either axial (a) or equatorial (e), (i.e. γ-HCH (Figure 1.8) is aaaeee (Figure 1.7). HCHs are produced as a technical mixture of eight isomers denoted by Greek letters α, β, δ, γ, ε, η, and ϕ (Figure 1.8) (Willett *et al.* 1998). Only the five isomers α, β, δ, γ, and ε are stable enough to be found in technical formulations (Li 1999). The α- isomer exists as two enantiomers and is a racemate in technical HCH. It is also worthy to note that conflicting designation of isomer identifiers occurs in the literature. Willet *et al* (1998) designated the η- isomer as *aaeaee* and

Plimmer (2001) described the same isomer as *aeaaee* (Figure 1.7). The composition of technical HCH varies and some percent composition by isomer is presented in Table 1.3. The foci of this section are the α-, β-, and γ-isomers.

1.5.1 History

Hexachlorocyclohexane was first synthesized in 1825 by Michael Faraday (Smith 1991a; Li 1999). The reaction proceeds via radical photochlorination when chlorine gas is bubbled through benzene. The discovery of HCH as an insecticide occurred during the 1940s (Li *et al.* 2002a) and it was subsequently used under various names including BHC (benzene hexachloride) and 666 (USEPA 1980). The insecticidal properties of HCH were not attributed to the γ- isomer until 1945 (Smith 1991a). HCH enriched in the γ- isomer by at least 90% is known as lindane (ATSDR 2005a). Technical HCH has been formulated as concentrates, dusts, cords, sprays, and seed treatments (Smith 1991a). Many more formulations of lindane were manufactured: concentrates, aerosols, sprays, dusts, powders, wood preservatives, cords, and seed treatments (Smith 1991a). HCH has been used in the production of fruit and vegetable crops, tobacco and as well as Christmas trees (Li 1999; ATSDR 2005a). Other areas where HCH has found use are the control of malaria and other vector borne diseases, grasshoppers, wireworms and other soil dwelling insects (Smith 1991a). Due to the extreme environmental and biological persistence various countries restricted the use of HCH: Canada in 1971, USA in 1974, China in 1983, USSR in 1990, Mexico in 1993, Australia in 1994, and India in 1990 for agricultural use (Li 1999). In Canada and the United States, lindane is still used as a seed dressing (ATSDR 2005b), and as a topical treatment for scabies and lice (ATSDR

2005a). The application of HCH for agricultural purposes may have involved the technical mixture or a mixture enriched with γ-HCH.

1.5.2 HCH Production

The global production and use of HCH is difficult to determine for a number of reasons. First, no central register exists for HCH production or sales, thereby necessitating the use of multiple sources (Voldner *et al.* 1995). Second, some countries maintained no or proprietary records and therefore data are unavailable (Willett *et al.* 1998). Third, where records of HCH application and sale were maintained it may be ambiguous whether active ingredient or mixture is the reported value (Voldner *et al.* 1995). Despite the inherent difficultly, attempts have been made to determine the temporal and spatial global distribution of hexachlorocyclohexanes.

Li (1999) reviewed information regarding the production/usage, registration status, and residue concentrations of HCH for numerous countries. Although North America, most of Europe, the USSR, Japan, China, and Australia had data available for all three areas, a majority of records were incomplete and required linear interpolation to account for missing temporal data. The only records requiring minimal temporal interpolation were those of China and Japan (Li 1999). Elucidating the usage of HCH was complicated by inconsistent recording methods such as: total HCH, total content by isomer, total application by formulation, or total active ingredient (Willett *et al.* 1998; Li 1999). The latter reporting method is further complicated since various countries define active ingredient differently (Li 1999). Batch differences for technical HCH reported in the literature also highlight the variability in recording application amounts (Table 1.3). It is possible to correlate production records with sediment cores, as this has been demonstrated for DDTs in Lake Ontario (Section 1.7.4). No attempt to correlate HCH sediment records to those of production are proposed here.

1.5.3 HCH in the environment

Much like DDTs, HCHs are ubiquitous throughout the environment. HCHs may be transported through the troposphere, or via ocean currents (Li *et al.* 2002a). Transport processes are based on physicochemical properties presented in (Table 1.1). In technical HCH the α- β- and γ- isomers account for approximately 70% of the mixture (Table 1.3). For this reason they are the isomers most often detected in environmental samples.

1.5.3.1 Long Range Transport of HCH

Various models of HCH transport to polar-regions have been proposed. Wania *et al.* (1995), using the model described on page 38, demonstrated the movement of γ-HCH toward polar regions. Four years after the emission of γ-HCH to the environment, an estimated 80% of γ-HCH was distributed to the marine environment.

It should be mentioned that despite relatively minor variations in structure between isomers of HCH (Figure 1.8), the resulting physical properties greatly affect the method of translocation in the environment. Li *et al.* (2002b) examined the different routes of transport between α-HCH and β-HCH. Classic cold condensation was observed, where α-HCH partitioned from the atmosphere to the cold waters of the arctic. Beta-HCH did not exhibit similar behaviour; a lower Henry's law constant (HLC) meant that β-HCH was scavenged from the atmosphere by rain and deposited to the ocean.

1.5.3.2 Microbial Degradation of HCH

Determining half-lives of HCHs in environmental compartments is important in elucidating HCH losses from areas of application. Most studies on soil residence time of HCHs have focused on γ-HCH. Loss of HCHs from soil may occur by numerous routes, including volatilization, microbial degradation, and uptake by plants.

Physicochemical properties (Table 1.1) such as vapour pressure are important to the movement of HCHs from areas of application. β-HCH has the lowest vapour pressure and is often detected at elevated concentrations relative to α-HCH in soils where the technical mixture has been applied (Li *et al.* 2002a). The elevated concentration of β-HCH, compared to other HCHs, is a product of low vapour pressure and resistance to microbial degradation (Li *et al.* 2002a).

Hexachlorocyclohexanes in soil can be transformed by microbial degradation. A study by Kumar *et al* (Kumar *et al.* 2006) investigated the loss of HCH isomers from soil inoculated with *Pseudomonas aeruginosa* ITRC-5. Losses of >98% α-, >98% γ-, 17% β-, 76% δ-HCH were observed after 15 days. Quintero *et al* (2005) reported the degradation of α- and γ-HCH from an anaerobic slurry in 20 to 40 days. The same system required at least 120 days to degrade the δ- and β-isomers. In the preceding studies, β-HCH was determined the most resistant isomer. The spatial orientation of chlorines in the equatorial position is the likely cause of β-HCH's remarkable resistance to most microbial degradation (Willett *et al.* 1998; Li *et al.* 2002a). β-HCH is not impervious to bacterial degradation. There is evidence a co-culture of *Dehalobacter* and *Sedimentibacter* is able to metabolize β-HCH through successive dichloroelimination reactions producing benzene or chlorobenzene. In this co-culture, the degradation rate decreased as the number of axial chlorines increased (van Doesburg *et al.* 2005).

Microorganisms from the North Sea have also show the ability to degrade α-HCH enantioselectively. Hühnerfuss et al (Hühnerfuss *et al.* 1992) demonstrated enantioselective degradation of α-HCH, where the (+)- enantiomer was favoured over that of the (-)- enantiomer. It was interesting to note that the degradation product, β-pentachlorocyclohexene (β-PCCH), produced from (+)-HCH was more favoured for further degradation than (-)-HCH or its corresponding β-PCCH enantiomer (Ludwig *et al.* 1992).

Calvelo Pereira *et al* (2006) demonstrated β-HCH bioaccumulation in plant tissues. Despite only compromising 38% of the applied mixture, β-HCH made up 70%, 67%, and 63% of total isomers in roots, stems, and leaves. The leaves were determined to have the highest concentration of β-HCH. The bioaccumulation of β-HCH by vegetation may contribute to increasing the observed half-life.

Determination of HCH isomers in soils may be complicated by isomerization. Malaiyandi *et al* (1984) reported the photoisomerization of γ-HCH to α-HCH in the presence of ferric-ferrous salts, and Deo *et al* (1980) reported the isomerization of β-HCH to δ-, α- and γ-HCH in sterile deionized water. Although photoisomerization would only occur at the soil interface, thereby being negligible, it may still play a minor role in the determination of specific isomers.

The preceding routes of elimination are dependent upon various properties of the soil. Some of these properties include: soil composition, ground coverage, temperature, moisture content, pH, and biological activity. Due to the high variability of factors affecting soils, the half-life determination is highly variable. Studies have reported half-lives of 4 weeks (Johri *et al.* 1996) to 120 days (Bintein *et al.* 1996). Lichtenstein *et al* (1959) reported half-life of lindane in turf soils at 11 years. Yet the method used to quantify required the conversion of HCH to a product that could be measured photometrically (Lichtenstein *et al.* 1956), and as such it is not possible to contribute the persistence to a specific isomer. The ranges presented highlight the difficulty in determining half-lives of HCHs in the global environment.

1.5.4 Toxicological effects of HCH

Although γ-HCH is the only isomer to exhibit any insecticidal activity, all HCHs are considered toxic. HCHs have been shown to have cytotoxic effects; the δ- isomer is the most cytotoxic followed by γ-, α-, and β- which has very little cytotoxic effect (Rosa *et al.* 1996). Much research has gone into the toxicology of HCHs, especially the γ- isomer. Generally the route of exposure to HCHs is through absorption from the lungs, the gastrointestinal tract (GIT), or the skin (Smith 1991a). Absorption through skin is highly variable, with certain areas such as face, forehead, and neck being more conducive to absorption than the hands or feet (Feldmann *et al.* 1974).

1.5.4.1 Toxicity of α-HCH

The α- isomer is unique amongst HCHs since it is the only chiral isomer (Figure 1.8). The brain appears to be the target of α-HCH deposition. A higher affinity of the α-isomer towards myelin was postulated by Stein *et al* (1980), although no mention of enantiomers specificity was made. A dose study of rats, Ulrich *et al* (2001), has shown high enantiomeric ratios (ERs) in the brains after 1 and 24 hours. The increase in the (+) enantiomer was attributed to selective uptake across the blood brain barrier and not the product of enantioselective metabolism.

When subcutaneously injected, α-HCH was observed to cause tremors and loss of coordination in mice (Smith 1991a). It should be noted that α- isomer counteracts the effect of the γ- isomer, and when administered in the same dosage the likelihood of mortality decreases (Smith 1991a).

1.5.4.2 Toxicity of β-HCH

Beta-HCH bioaccumulates quite readily, as mammals lack effective mechanisms with which to eliminate it (Li *et al.* 2002a). In a study of former workers from a lindane-producing plant, a half-life in blood of 7 years was determined for β-HCH (Jung *et al.* 1997). A separate study by Nigam *et al* (1986) showed workers directly exposed to HCHs had serum concentrations 2.5 times higher than workers not directly exposed to HCHs. Calculated bioconcentration factors (BCFs) of β-HCH in human adipose tissue have been reported as 25 times greater than those of the next closest isomer (Geyer *et al.*

1987) (Table 1.2). A study by Bigsby *et al.* (1997) demonstrated the mobilization of fat reserves in mice serve as a source of β-HCH.

β-HCH has been shown to exert its effects as a central nervous system (CNS) depressant and estrogen mimic. The CNS is depressed by β-HCH as illustrated by mice subcutaneously injected with β-HCH exhibiting lameness and flaccidity (Smith 1991a). It should be noted that the β- isomer counteracts the effect of γ-HCH when administered in the same dosage thereby decreasing the likelihood of mortality (McNamara *et al.* 1948b; McNamara *et al.* 1948a). Diet studies of female rats fed 50 mg/kg for 5 days showed significantly increased uterine weights (Loeber *et al.* 1984), indicative of estrogenic activity. Male medaka fish exposed to water borne β-HCH at concentrations 0.1-1 mg/L began producing an egg yolk precursor protein, usually only present in females (Wester *et al.* 1986).

1.5.4.3 Toxicity of γ-HCH

The γ-isomer of HCH (Figure 1.8) also known as lindane is the only isomer shown to have insecticidal properties. The mode of action of γ-HCH is stimulation of the CNS leading to hyperexcitability and violent convulsions, which may result in death (Tusell *et al.* 1987). Convulsions associated with acute poisoning are likely due to non-competitive GABA antagonism (Pomes *et al.* 1993). Other symptoms of acute lindane poisoning include tremors, ataxia (inability to coordinate voluntary muscular movements), stimulated respiration, and prostration (complete physical or mental exhaustion) (Ecobichon 2001). The potential for chronic poisonings due to γ-HCH appears insignificant; via intravenous exposure Feldman *et al* (1974) reported a half-life in humans of 26 hours.

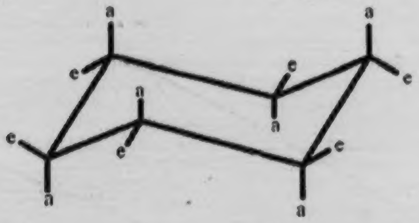

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Figure 1.7: Chair conformation of cyclohexane. Cyclohexane backbone showing axial (a) and equatorial (e) positions

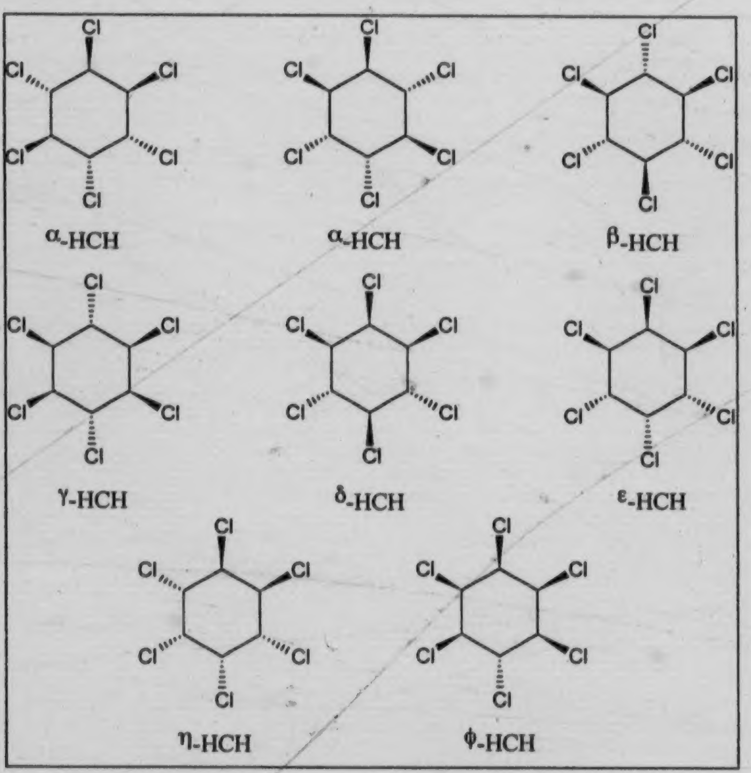
Cl
α-HCH
α-HCH
β-HCH
γ-HCH
δ-HCH
ε-HCH
η-HCH
ϕ-HCH

Figure 1.8: Isomers of hexachlorocyclohexane (HCH)

Table 1.1: Physical Properties of HCH Isomers (Mackay *et al.* 1992)

	α-HCH	β-HCH	γ-HCH	δ-HCH
Melting Point	158	309	112	139
Vapour Pressure (Pa at 25°C)	1.8x10^{-2} ± 3.2x10^{-2}	4.21x10^{-5} ± 0.06x10^{-5}	7.61x10^{-3} ± 8.90x10^{-3}	2.27x10^{-3} ± 2.00x10^{-3}
Log K_{ow}	3.53 (Verhaar *et al.* 1992)	3.89 ± 0.14	3.69 ± 0.47	4.12 ± 0.02

Table 1.2: Calculated Bioconcentration Factors in Human Adipose Tissue (Geyer *et al.* 1987)

Isomer	BCF_{Lipid} mean±S.D. (Range)	N
α	20.0±8 (11.5-32.5)	5
β	527±140 (310-744)	7
γ	18.6±9 (10.4-32.5)	7
δ	8.5	1

Table 1.3: Composition of Technical HCH and Lindane

α-HCH	β-HCH	γ-HCH	δ-HCH	ε-HCH	Source
60-70%	5-12%	10-12%			(Iwata *et al.* 1993)
55-80%	5-14%	8-15%	2-16%	3-5%	(Li 1999)
60-70%	5-12%	10-12%	6-10%	3-4%	(Willett *et al.* 1998)
		13%			(Plimmer 2001)
		Lindane: 90%			(Li 1999)

1.6 Chlorinated Cyclodienes

Chlorinated cyclodienes include components of technical chlordane as well as associated degradation products. Technical chlordane is a complex mixture of more than 140 compounds (Dearth *et al.* 1991b). This section will focus on the following components of technical chlordane: *cis*-chlordane, *trans*-chlordane, heptachlor, *cis*-nonachlor, *trans*-nonachlor, and the related degradation products heptachlor-*exo*-epoxide and oxychlordane. All cyclodienes will preferentially partition to octanol, as indicated by measured log K_{ow} values (Table 1.5), and should therefore bioaccumulate.

1.6.1 Chlordane Production

Chlordane was first produced in 1945 (Kearns *et al.* 1945). The synthesis is carried out by the Diels-Alder reaction of hexachlorocyclopentadiene with cyclopentadiene. The resulting chlordene is then chlorinated at elevated temperature and pressure to produce the technical chlordane mixture. The last known large-scale producer of chlordane in North American was the Velsicol Chemical Co. (ATSDR 1994). The isomeric composition of chlordane varies depending upon the batch or synthesis method. The weight percent compositions of some technical chlordane mixtures are presented in (Table 1.4). AG chlordane is an enriched mixture of *cis*- and *trans*-chlordane, 70% and 25% respectively (BCPC 1974). As many as 73 commercially available formulations of chlordane, alone or in combination with other insecticides, were registered for use (NRCC 1973). Reported Canadian sales of chlordane between the years 1957 and 1973 ranged from 9 to 132 thousand kilograms per year (NRCC 1973). The cancellation of chlordane's registration as a pesticide by the United States Environmental Protection Agency (EPA) occurred between the years 1983 and 1988 (McGaughy *et al.* 1997). Although chlordanes are no longer registered for use, they continue to be produced in North America for export (ATSDR 1994).

1.6.2 Chlordane Use and Persistence

Chlordane was used as a soil control method for soil pests such as rootworms, weevils, wireworms, grubs, subterranean cut worms (Canada 1997), and termites (ATSDR 1994). Chlordane is a non-systematic stomach and contact insecticide, and is considered non-phytotoxic at insecticidal concentrations (BCPC 1974). Technical chlordane composition plays a role in determining the environmental half-life, and since it was applied as a ground-based pest control method, other factors such as soil character, moisture, weathering, and microbial activity yield a half-life ranging from 10 to 20 years (Dearth *et al.* 1991b).

1.6.3 Chlordane Toxicity

Chlordanes are believed to be carcinogenic towards humans. A study by Woods *et al.* (1989) reported an increased risk of non-Hodgkins lymphoma among farmers reporting regular use of chlordane. The study was limited because the frequency of use and the duration of exposure for each farmer were not known. Results from numerous toxicological studies of chlordanes on various mice and rats and reviewed by Epstein (1976) highlighted a plethora of deleterious health outcomes, some of which were: hyperplasia (abnormal increase in the number of cells in an organ or tissue), benign hepatomas (non-cancerous liver tumor), and hepatic carcinomas (cancer of the liver that occurs on the surface tissue). The mounting evidence of such studies led to the EPA classification of technical chlordane as Group 2B, suspected human carcinogen (McGaughy *et al.* 1997). In addition to increased cancer risk other effects are associated with chlordane exposure. A study by Welch *et al.* (1971) demonstrated decreased reproductive success in female mice dosed with chlordane once a week for three weeks. As well, an epidemiological investigation of humans exposed to chlordane, aldrin and heptachlor treated homes showed incidence rates of anemia, migraine, ovarian and uterine disease, dermatitis and skin tumor where significantly increased (Menconi *et al.* 1988).

1.6.4 Heptachlor

Heptachlor (Figure 1.9) a minor product formed in the production of chlordane (Table 1.4), has also been produced as the majority constituent of chlordane. This formulation consisted of approximately 72% heptachlor with the remainder usually comprised of *trans*-chlordane, *cis*-chlordane, and nonachlors (Figure 1.9) (HSDB 2006a). This formulation was used to control cotton boll weevils, termites, and certain soil-inhabiting insects (HSDB 2006a). Heptachlor is persistent throughout the environment particularly because it is readily retained in soils. Although volatilization from soil is considered a significant source of heptachlor to the environment, it is attenuated by adsorption to soil. An example of this is a study reported by Glotfelty *et al.* (1984) where 93% of heptachlor remained after 167 days if incorporated into soil, yet when applied to grass 10% remained after 7 days. Heptachlor is classified as a group 2B carcinogen (suspected human carcinogen) by the EPA (IARC 2001). In studies, which orally exposed mice to heptachlor, technical heptachlor, or a mixture of heptachlor and heptachlor epoxide, neoplasms and carcinomas were observed (Epstein 1976). The EPA proposed the cancellation of most registered uses of heptachlor in 1974, due to its suspected carcinogenicity. However, not all treatments were immediately cancelled; corn, seed, citrus, and pineapple where phased out during the five-year period preceding July 1, 1983 (ATSDR 1994).

1.6.5 Heptachlor-*exo*-epoxide, Oxychlordane, *cis*- & *trans*-Nonachlor

Heptachlor epoxide and oxychlordane are metabolites of chlordane, whilst nonachlors are minor impurities present in technical mixtures of chlordane. These minor components are of significant interest since they, as with the other major chlorinated cyclodienes, possess values of log K_{ow}, which allow them to bioaccumulate (Table 1.5) (Figure 1.6). An example of bioaccumulation is a survey study of nursing mothers, which detected heptachlor epoxide and oxychlordane in 100% of breast milk samples and *trans*-nonachlor in 98% of the samples. The mean concentrations, on an extractable lipid basis, were 35, 59 and 81 ppb respectively (Takahashi *et al.* 1981). Dearth *et al.* (1991a) determined the geometric mean concentration of the same three compounds in breast adipose tissue as 48, 88, and 120 ng/g of fat, respectively.

1.6.5.1 Heptachlor-*exo*-epoxide

The oxidation of heptachlor leads to the formation of the metabolite heptachlor epoxide (Melnikov 1971). Heptachlor epoxide (Figure 1.9) is readily formed from heptachlor under the action of soil microorganism and enzymes in higher organisms (Melnikov 1971). It is hypothesized that much of the toxicity associated with heptachlor is due to the formation of the more toxic metabolite heptachlor epoxide (Epstein 1976). Clarke *et al.* (1981) reported that heptachlor epoxide was ten times more toxic to dairy calves than heptachlor, when administered orally. Strong adsorption to soil and extreme resistance to biodegradation (HSDB 2006c) means that heptachlor epoxide persists in areas of chlordane or heptachlor application.

1.6.5.2 Oxychlordane

Oxychlordane (Figure 1.9) is considered a dead-end metabolite (metabolite after which no further metabolism occurs) of chlordane and is indicative of chlordane exposure (HSDB 2006b). In a study by Mes *et al.* (1984) there was a significant decrease in oxychlordane in human breast milk over a 98-day lactation cycle. The bioaccumulation of oxychlordane in the infant led to a projected contaminant level of an adult (body fat normalized) within three months of suckling initiation.

1.6.5.3 *cis*- & *trans*-Nonachlor

Nonachlors are minor impurities present in technical chlordane (Table 1). Nonachlors may have either *cis*- or *trans*- configurations (Figure 1.9). Nonachlors are considered recalcitrant compounds, especially with respect to humans (Ogata *et al.* 1991). *Trans*-nonachlor is 13 times more bioaccumulative in humans than *cis*-nonachlor (Dearth *et al.* 1991a). One of the first routes through which an infant is exposed to *trans*-nonachlor is *via* suckling. As with oxychlordane an infant will bioaccumulate *trans*-nonachlor and increase its body burden to that of an adult (Mes *et al.* 1984). A study examining the metabolic fate of *trans*-nonachlor in rats showed that *trans*-chlordane is a metabolite, whilst in humans this is not the case (Tashiro *et al.* 1978).

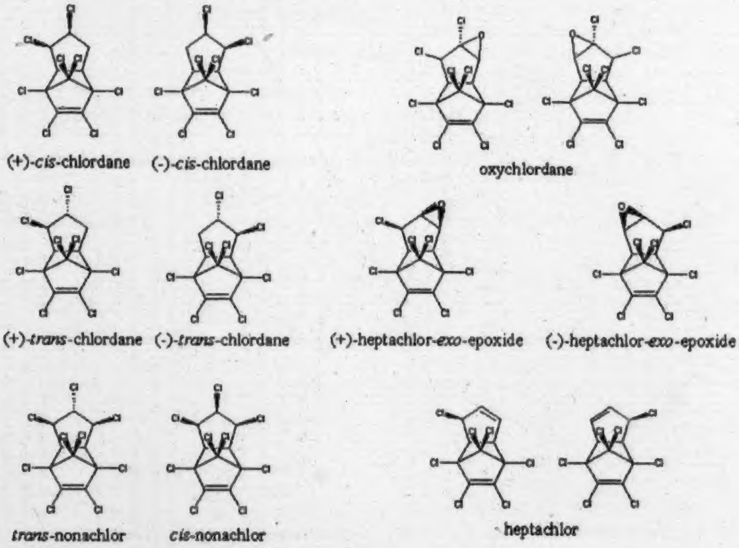
(+)-*cis*-chlordane
(-)-*cis*-chlordane
oxychlordane
(+)-*trans*-chlordane
(-)-*trans*-chlordane
(+)-heptachlor-*exo*-epoxide
(-)-heptachlor-*exo*-epoxide
trans-nonachlor
cis-nonachlor
heptachlor

Figure 1.9: Chlorinated cyclodienes

Table 1.4: Weight % composition of technical chlordane. HEPT: heptachlor, TC: *trans*-chlordane, CC: *cis*-chlordane, TN: *trans*-nonachlor, CN: *cis*-nonachlor

	HEPT	TC	CC	TN	CN	Source
% by weight	10	14.5	13	6	1.6	(Buser *et al.* 1993)
	6	10	9.2	6	1.7	(Dearth *et al.* 1990)
	1	25	70			(BCPC 1974; Tafuri *et al.* 1977)
		60 – 75				(Melnikov 1971)

Table 1.5: Log K_{ow} values of selected cyclodienes

	Log K_{ow}	Source
heptachlor	6.10	(Simpson *et al.* 1995)
	5.44	(Garten *et al.* 1983)
heptachlor epoxide	5.40	(Garten *et al.* 1983)
trans-chlordane	6.22	(Simpson *et al.* 1995)
cis-chlordane	6.10	(Simpson *et al.* 1995)
trans-nonachlor	6.35	(Simpson *et al.* 1995)
cis-nonachlor	6.08	(Simpson *et al.* 1995)

1.7 DDT

DDTs (Figure 1.10) are a class of chlorinated compounds based on the structure of 1,1,1-trichloro-2,2-bis-(phenyl)ethane. The composition of technical DDT varies depending on reaction conditions, with an approximate composition of 77.1% *p,p'*-DDT, 14.9% *o,p'*-DDT, 0.3% *p,p'*-DDD, 0.1% *o,p'*-DDD, 4.0% *p,p'*-DDE, and 0.1% *o,p'*-DDE (Smith 1991b).

1.7.1 History of DDT

DDTs were originally synthesized in 1874 by Othmar Zeidler (Metcalf 1973; Smith 1991b). Zeidler's synthesis was carried out by reacting 225 parts of chlorobenzene with 147 parts of chloral with 1000 parts of sulphuric acid with stirring (West *et al.* 1950).

The insecticidal properties were not discovered until 1939 when DDT was synthesized by Paul Müller at J. R. Geigy S.A. (West *et al.* 1950; Smith 1991b). The discovery of DDT’s insecticidal properties was the result of seven years of work by Geigy researchers, who were searching for an insect stomach poison to control moths (West *et al.* 1950).

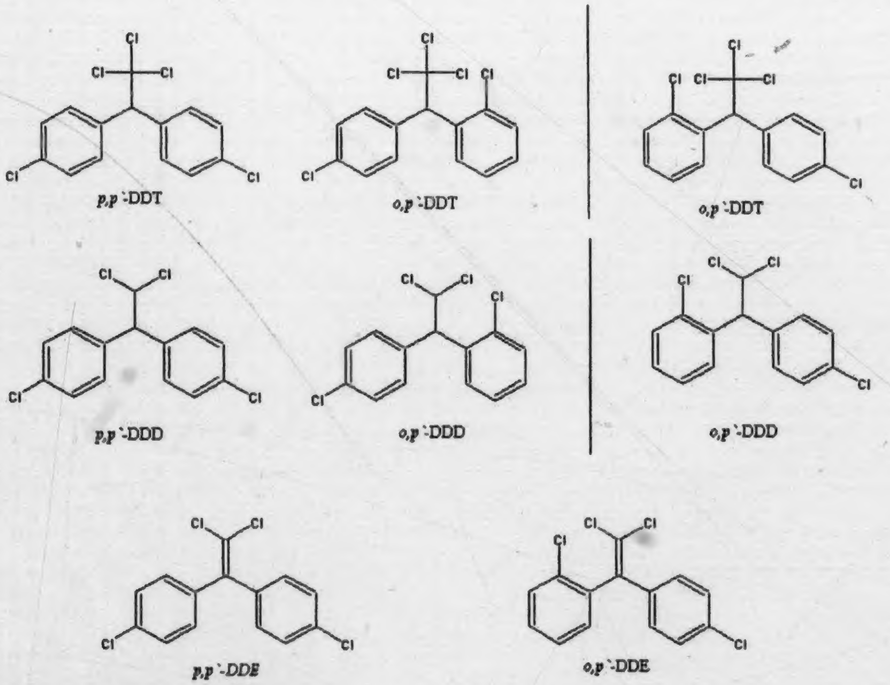

Figure 1.10: Structures of DDT

Early research into the application of DDT as an insecticide was tested by researchers at Giegy for a variety of insects including: the flea beetle, carrot-fly, louse, mosquito, and housefly (West *et al.* 1950). These tests were mainly focused on using DDT as a contact insecticide and the effect of different formulations and delivery methods. DDT has been applied in any one of several different forms: powder, aqueous spray, solution, emulsion, and aerosol. The powder formulation was often used for dusting or spraying. Powders were made when crystalline DDT was mixed with any number of substances such as talc (magnesium silicate), china clay (hydrated alumina silicate), gypsum with amorphous silica, or kieselguhr (diatomaceous earth) with amorphous silica. Generally the particle size of commercial DDT powders produced in the U.S.A. was 4.1 µm (West *et al.* 1950). Powdered mixtures have also been the basis for aqueous sprays of DDT. Given the hydrophobic nature of DDT, the use of aqueous sprays enabled maximum DDT dispersion at minimal cost, especially from dusting planes. Solutions of DDT and hydrocarbons, especially kerosene, were frequently used for domestic spraying. When need for concentrated formulations arose they were often made of 35% DDT in either methyl-cyclohexanone or benzene. Emulsions found favour during WWII as many solvents were scarce, and emulsions allowed for wide dispersion of DDT much like aqueous sprays. Aerosol bombs were used to treat closed areas. Formulations often utilized dichlorodifluoromethane (Freon 12) and methylene chloride to solubilize DDT. By the time DDT was exported to the United Kingdom and the U.S.A. it was heralded as a promising tool to aid humanity in its fight against disease spreading vectors. Further tests conducted in the U.K. and U.S.A. backed up the promising results obtained by Geigy scientists. DDT's low cost and potency towards disease-carrying pests led to its widespread production and use by the military (West *et al.* 1950). DDT was used since 1942 to control pests and malaria in and around military bases and ports. In 1945, DDT became available for commercial use and numerous other applications, including its addition to textiles, linoleum, paint, paper, and rubber occurred.

1.7.2 DDT Production

As is the case with many persistent pollutants, it is difficult to precisely know the quantity of DDT produced. Some countries maintained no or proprietary records; therefore reliable data is difficult to obtain, even in a single country. According to Zhang *et al.* (2002) China accounted for 30% of the global DDT production at 400 000 tonnes, while Li *et al.* (1999) put the production at 270 000 t. Worldwide production of DDT is estimated at 2 to 2.6 million tonnes (Voldner *et al.* 1995; Corsolini *et al.* 2006).

1.7.3 DDT Ban

Widespread use of DDTs was eventually linked to eggshell thinning in predatory avians (Anderson *et al.* 1968; Lincer 1975). Eggshell thinning was apparently facilitated by increased concentrations of DDE caused by biomagnification (Hickey *et al.* 1966; Lincer 1975). Public pressure and concern over public safety led to the subsequent U.S. Environmental Protection Agency (EPA) ban of DDT on December 31, 1972 (EPA 1972). China continued to use DDT until the mid-1980s (Voldner *et al.* 1995). The U.S.S.R. officially prohibited DDT in 1971, although exemptions for its application continued for 10 years (Kundiev 2000). Depending on the source, DDT has been banned in Canada numerous times: 1989 (EC 1992), 1972 or 1969 (Gilkeson *et al.* 2006a). There is some misinterpretation about the dates associated with DDT's ban in Canada because DDT was unregistered before it was banned and provincial bans were sometimes exerted before the federal ban. Despite bans on DDT in some countries, due to the low production cost and effective vector control properties (Najera *et al.* 2003), it maintains viable applications in certain areas of the world (WHO 1995). One such area of current application is East Africa where it is used to control malaria and meet agricultural demands (Kidd *et al.* 2001). The semivolatile nature of DDTs means that atmospheric transport to areas far from the site of application is significant.

Table 1.6: Physical Properties of DDT compounds.

	M.W.	M.P.	Log K_{ow}	Henry's Law constant @ 20 °C
p,p'-DDT	354.49 (a)	109 (a)	6.91 (a)	2.36 (c)
p,p'-DDE	318.03 (a)	89 (a)	6.51 (a)	7.95 (c)
p,p'-DDD	320.05 (a)	109-110 (a)	6.02 (a)	0.64 (c)
o,p'-DDT	354.49 (a)	74.2 (a)	6.79 (a)	
o,p'-DDE	318.03 (a)	75-78 (b)	6.00 (a)	2.54 (c)
o,p'-DDD	320.05 (a)	76-78 (a)	5.87 (a)	0.64 (c)

(Sources: a:(ATSDR 2002), b: (AccuStandard 2005), c: (Suntio *et al.* 1988))

1.7.4 Long Range Transport of DDT

Even though DDT has been banned/restricted in numerous high latitude countries (EPA 1972; EC 1992), it is still ubiquitous throughout the environment. This is due to long-range transport (LRT), which enables DDTs to be transported to higher latitudes (Ottar 1981; Bidleman *et al.* 1992; Bard 1999). Various models have been hypothesized in an attempt to determine global transport of many pollutants including DDTs. Using physicochemical properties such as: melting point, molecular mass, vapour pressure, solubility, Henry's law constant, and log $K_{ow,}$ Wania *et al.* (1995) calculated the movement of DDT thorough the environment. The model partitioned the global environment into nine zones each containing six compartments with multiple temperature dependent transport and reaction processes. Using a utopian initial state, the northward distillation of DDT from a northern tropical latitude (12.4°N) to a northern boreal latitude (58.3°N) was calculated (Wania *et al.* 1995). Due to the phenomena of global distillation DDT exposure is still of significance even in areas of discontinued use.

A study by Eisenreich *et al.* (1989) attempted to determine the inventory of various pollutants in the sediment of Lake Ontario with respect to North American production. After accounting for sedimentation rate and compaction it was determined that inputs of DDT were in agreement with historical production data. DDT accumulated from 1945, peaking through 1958 to 1960 and then declining. A subsequent study by Wong *et al.* (1995) demonstrated that sediment records of contaminant input were preserved below the layer of biological perturbation and that diffusion was not significant.

1.7.5 Toxicological Effects of DDT

Since DDT's creation at J. R. Geigy S.A., a host of studies on the toxicity of DDT as both single isomers and mixtures have been carried out. Early work focused mainly on the effectiveness of application methods against vectors of disease (West *et al.* 1950). Since a majority of DDT released to the environment has been as a technical mixture, numerous isomers are often found in environmental compartments and biological tissues. Therefore, it is difficult to attribute specific toxic effects to any singular isomer. Despite this knowledge, toxicological studies have focused on single isomers. Due to it being a majority constituent of technical DDT, *p,p'*-DDT was initially the focus of early toxicological studies.

1.7.5.1 *p,p'*-DDT

The DDT isomers *o,p'*-DDT and *p,p'*-DDT make up approximately 80% of technical DDT. Generally, DDT resides in the environmental compartment in soils and sediments due to its hydrophobic nature. The residence half-life of DDT in soils can vary from 2 to 15 years, depending on the soil matrix and the microbial content (Edelbrock *et al.* 2005).

DDT is rapidly degraded by 253 nm UV light (Mosier *et al.* 1969); however, wavelengths lower than 290 nm do not occur near the Earth's surface (Schwarzenbach *et al.* 1993), so it is unlikely that direct photolysis will degrade DDT to a significant extent, allowing it to migrate through the troposphere.

1.7.5.2 *o,p'*-DDT

The presence of an asymmetrically substituted carbon makes *o,p'*-DDT is a chiral molecule (Figure 1.10). The resulting (-) and (+) enantiomers have different biological properties and the toxicokinetics of each must be considered separately. It has been demonstrated that the *levo* (-) enantiomer of *o,p'*-DDT competitively inhibits the binding of 17β-estradiol (McBlain 1987b). The estrogenic activity has been demonstrated as *o,p'*-DDT supports the growth of an estrogen responsive tumour in a dose dependant manner, specific to *o,p'*-DDT (Robison *et al.* 1985). In a study by Kramer *et al* (1995), (-)-*o,p'*-DDT showed higher estrogenic activity than (+)-*o,p'*-DDT. Heinricks *et al* (1971) demonstrated the advancement of puberty, persistent vaginal estrous, and reproductive abnormalities in female rats due to the administration of *o,p'*-DDT.

However, after the ban on DDT in the 1970s the foci of DDT toxicological studies have shifted to the degradation products, DDD and DDE. Despite DDDs and DDEs accounting for less than 10% of technical DDT (Smith 1991b) they are significant when considering DDTs in the environment. The reductive dechlorination of *p,p'*-DDT and *o,p'*-DDT, under anaerobic conditions, leads to the production of *p,p'*-DDD and *o,p'*-

DDD as major end products (Zoro *et al.* 1974; You *et al.* 1996). Under aerobic conditions the same precursors produce the associated DDEs (Garrison *et al.* 2000).

1.7.6 DDD Toxicological Effects

The two main DDT isomers of consequence are DDD and DDE. Technical DDT contains less than 1% DDD (Smith 1991b). DDD is introduced to the environment through three routes: firstly, as a trace constituent of technical DDT, secondly, through its use as the insecticide TDE, and lastly as a DDT degradation product. DDD, like DDT, can have either symmetrically are asymmetrically substituted phenyl rings, yielding either *p,p'*-DDD or *o,p'*-DDD respectively. The three resulting isomers *p,p'*-DDD, (+)-*o,p'*-DDD, and (-)-*o,p'*-DDD must be considered separately when determining the toxicological effects of DDD. Andrenocortical carcinoma has been treated with *o,p'*-DDD (Wooten *et al.* 1993), although no differentiation with respect to enantiomers was mentioned. The degradation of DDD occurs by the reductive dechlorination of DDT at the trichloro-carbon moiety.

1.7.7 DDE Toxicological Effects

DDE accounts for less than 5% of technical DDT (Smith 1991b). The introduction of DDE to the environmental compartment occurs mainly by two processes; firstly, as a minor constituent in technical DDT, and secondly as a product of metabolism or degradation. DDE is the most recalcitrant DDT isomer and considered a dead end product of DDT decomposition (Lin *et al.* 2007). That is not to say that it cannot be metabolized, as studies by Bergman *et al.* (1977) and Sundström *et al.* (1975) have shown that *p,p'*-DDE may be metabolized to 3-methylsulfonyl *p,p'*-DDE and 2-,3-,and 4-

hydroxy-*p,p'*-DDE. DDE is generally difficult to excrete and therefore burdens will increase throughout an organism's life. Generally, DDE exposure is likely to begin at the prenatal stage of development and increase until lactation subsides. Developmental effects associated with prenatal *p,p*'-DDE exposure in rats include: feminization of male rats, reduced sperm production, and delayed puberty onset (Edelbrock *et al.* 2005) In a study by Crellin *et al.* (1999) p,p'-DDE was found to affect progesterone synthesis. Progesterone is an important hormone required to initiate and maintain pregnancy. As the use of DDT in the agricultural and malaria control theatres continues, it will continue to be of environmental significance.

2 Trophodynamics of Organochlorine Pesticides in the aquatic food web of Lac La Biche, AB

2.1 Introduction

Lac La Biche, located in northern Alberta (54° 46' N, 112° 1' W), is part of Lakeland County and is situated in the natural boreal forest region. Two communities are found on the shores of Lac La Biche: Plamondon and the town of Lac La Biche, for a total population of approximately 7700. The quality of water in this lake has been degrading due to nutrient loading from increased development in the county, and over-fishing. Collapse of the commercial fishing industry caused by over-fishing of; northern pike (*Esox lucius*), lake whitefish (*Coregonus clupeaformis*), and walleye (*Stizostedion vitreum*) has facilitated the proliferation of forage fish species such as yellow perch (Vander Zanden *et al.* 2005). The increased abundance of forage fishes has allowed for establishment of double-crested cormorant colonies on the islands of Lac La Biche. Currently, these colonies of double-crested cormorants appear to be hindering the efforts to restock walleye in Lac La Biche (White *et al.* 2006). Directed population control of double-crested cormorants is being performed in an effort to allow the restocking to take hold. The eventual control of double-crested cormorants and rebuilding of walleye stocks in Lac La Biche will undoubtedly cause a change in the food web structure of Lac La Biche (Kidd *et al.* 1999).

Organochlorine contaminants analyzed in this study are pervasive throughout the global environment (Bidleman 1988; Bidleman *et al.* 1992). The input of these pollutants to the food web of Lac La Biche may be due to either long range transport from areas of current use or localized inputs, either current or historic. Often these pollutants are dispersed as technical mixtures and sites of recent exposure to technical mixtures exhibit an "isomeric signature" similar to that in the technical mixture. Technical mixtures contain, among other compounds, numerous structural isomers some of which may be racemic enantiomer pairs. As weathering of exposed areas occurs, the isomeric signature will be altered due to various processes. For example, volatilization of α-HCH and vapour scavenging of β-HCH (Li *et al.* 2002a) limit the rate at which these components are carried afield. Interactions with biological systems may change the isomeric signature and/or the enantiomeric fraction. Examining the amount and relative proportion of the isomers in the Lac La Biche food web it may be possible to determine the method of introduction to the ecosystem.

Chiral organochlorine contaminants such as α-HCH, *trans*-chlordane, *cis*-chlordane, heptachlor, and *o,p'*-DDT are introduced to the environment as racemic mixtures. The same does not necessarily apply to chiral degradation products such as heptachlor-*exo*-epoxide, oxychlordane and *o,p'*-DDD. By monitoring the enantiomeric fractions throughout the Lac La Biche aquatic food web, it may be possible to elucidate additional information about these compounds. This information may be useful in remediation, global modeling, toxicology, or to help understand previously unknown biotransformation capability.

The aim of this project is to collect relevant data regarding the chemical composition of the Lac La Biche aquatic food web. The data may be used to determine possible sources of contaminants to Lac La Biche, as well as elucidate any species dependent interactions within the food web. The Lac La Biche food web is likely to change due to human influence, and the research presented here serves as a beforehand account of how organochlorine pollutants distribute throughout the food web (trophodynamics), with particular attention to enantiomer fractions (EFs).

2.2 Experimental Procedure

2.2.1 Sample Collection

Samples were collected from Lac La Biche, AB at monthly intervals during the summer of 2004. Gill nets were used for the abstraction of northern pike (NRPK), walleye (WALL), white sucker (WHSC), lake whitefish (LKWH), and yellow perch (YLPR). Small minnow species such as spottail shiners (SPSH), cisco (CISC) and yellow perch were collected by seine net (Table 2.1).

Table 2.1: Number of analysed samples.

	Fillet / Breast / Composite Sample	Liver
NRPK	10	10
WALL	2	2
YLPR	10	2
WHSC	1	1
LKWH	3	2
DCCO	4	4
CISC	4	4
SPSH	3	N/A
DCCO Chick	3	4
EGG	3	3
SNAIL	1	N/A

Concurrent to gill net sampling, rod and reel were utilized to sample northern pike. Double crested cormorants (DCCO) were collected opportunistically by shotgun, double-crested cormorant eggs were also collected opportunistically. Upon collection, all samples were immediately measured and stored on ice, for no more than 10 hours, until such a time when they could be frozen. The sex of collected specimens was not determined.

2.2.2 Extraction

Prior to extraction specimen length and mass were recorded. Fishes were dissected by cutting up the belly from the dorsal fins to the bottom of the gills. The gastrointestinal tract (GIT) was discarded to avoid extraction of analytes in undigested food, and the liver removed and processed separately from the remainder of the carcass. A fillet knife was used to separate the muscular tissue from the scales prior to homogenization. Smaller-sized fish samples were counted, pooled and homogenized. All samples were partially thawed for homogenization, which was performed using a Waring blender. The samples were weighed by difference and transferred to a mortar and pestle containing anhydrous sodium sulphate (Tracepur ACS-grade, EMD chemicals, Gibbstown, NJ). Sodium sulphate had previously been ashed at 450°C for 3 hours. Samples were manually ground until a free flowing powder was obtained. Samples were quantitatively transferred to a glass soxhlet thimble (in house). All samples were spiked with 12 ng PCB-30 and PCB-204 (AccuStandard Inc. New Haven, CT), and 30 ng $^{13}C_6$ δ-HCH (Cambridge Isotope Laboratories Inc., Andover MA) to determine extraction recovery. Soxhlet extraction with pesticide grade (PG) dichloromethane (DCM) (Fisher Scientific) was carried out overnight. Sodium sulphate was added to each round bottom flask to control bumping.

Soxhlet apparatuses were quantitatively rinsed with DCM from the top and the DCM extracts filtered through a sintered glass funnels, each containing a 1-cm bed of ashed sodium sulphate. Extracts were concentrated to 1-2 ml using a rotary evaporator, and quantitatively transferred to a pre-weighed 12-ml glass screw cap vial. Lipid determination was performed gravimetrically using approximately 10% of the extract. The extract mass was measured before the removal of the aliquot and the aliquot mass was determined by difference. The percent lipid was determined gravimetrically and calculated using Equation 2.1.

$$\%\ Lipid = \frac{\frac{Extract\ (g)}{Aliquot\ (g)} \times Lipid\ in\ Aliquot\ (g)}{Sample\ (g)} \times 100\%$$

Equation 2.1: Lipid Determination

The remaining extract was concentrated to 1-2 ml under nitrogen. The volume of the extract was then doubled with the addition of PG hexane (Fisher Scientific).

2.2.3 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was performed upon the extracts. Each extract was added to the top of a column composed of 200-400 mesh Biobeads^{TM} (Bio-Rad Laboratories, Hercules CA). Lipids were eluted with 160 ml of 1:1 DCM/hexane (v/v). The extract was collected with 140 ml of 1:1 DCM/hexane (v/v) and solvent exchanged to hexane. A rotary evaporator was used to concentrate the extract to 3-5 ml, 25 ml of PG hexane was added and the process repeated twice. The extract was further concentrated to 1-2 ml and quantitatively transferred via subsequent hexane rinses to a 12-ml glass screw cap vial. The extract was concentrated to 1-2 ml under nitrogen.

2.2.4 Alumina/ Silica Chromatography

Alumina/silica columns were prepared by wet packing, with PG hexane, a 1-cm bed of sodium sulphate, 3 ± 0.03 g of 2% by weight deactivated silica gel (70–270 mesh, Aldrich Chemicals, Fair Lawn, NJ), 8.5 ± 0.08 g of 8.5% by weight deactivated alumina oxide (150 mesh, Aldrich Chemicals, Fair Lawn, NJ), and 1 cm of ashed sodium sulphate. The elution of the extract was carried out with hexane for fraction one (F1) total volume of 30 ml. Fraction two (F2) was eluted with 35 ml of 19:1 PG hexane/ PG acetone (v/v) and the column was allowed to go dry. Both fractions were concentrated to 1-2 ml and quantitatively transferred to 12-ml glass screw cap vials with PG hexane and further concentrated to 1-2 ml under nitrogen. Prior to analysis, extracts were transferred to 1.8-ml amber glass autosampler vials (Fisher Scientific), and spiked with 90 ng of the internal standard, tetrachloro-*m*-xylene (CAS number: 108-18-3, AccuStandard Inc., New Haven, CT) To facilitate PCB analysis PCB-166 was added to F1s as an internal standard (Morrissey 2007).

2.2.5 Fraction One Analysis

Detection and determination of chiral signatures of targets contained within F1 was performed using a HP 5890/5971 gas chromatograph/mass selective detector with electron impact ionization (70 eV). Selected ion monitoring (SIM) of three most abundant ions was utilized for the detection of DDTs, DDDs and DDEs. Injector port conversion of DDT was monitored by periodically injecting 2-ppm standards of *p,p'*-DDT or *o,p'*-DDT and determining areas of related peaks as per Foreman *et al.* (1997). Conversion of DDT was determined to be <1%. This loss is not considered significant, since the overall proportion of DDT in the samples was low enough that any isomerization of DDT was below the limit of detection. Chiral analysis was performed using a BGB-172 column (30 m × 0.25 mm × 0.18 µm, BGB Analytik, Adiswil, Switzerland) connected in tandem using a 0.1 - 0.25 mm mini union (SGE Inc., Austin, TX) to a Rtx-5 column (15 m × 0.25 mm i.d. × 0.10 µm, Restek, Bellefonte, PA). Samples were analyzed using the following oven program: 60°C for 2 min, 15°C min^{-1} for 10 min, 1°C min^{-1} to 225°C and held for 10 min. The injector and transfer line were maintained at 200°C and 280°C respectively. Helium (prepurified) carrier flow was electronically maintained at 1 ml min^{-1}.

2.2.6 Fraction Two Analysis

Target analytes contained within F2 (α-, γ-, β-hexachlorocyclohexanes, heptachlor, oxychlordane, heptachlor-*exo*-epoxide, *trans*- and *cis*-nonachlors, *trans*- and *cis*-chlordanes) were detected using an Agilent 6890/5973 gas chromatograph/mass selective detector operating in negative chemical ionization mode (NCI). The BGB-172/Rtx-5 tandem column setup, described above, was used for F2 analysis using a different temperature program: 60°C for 1 min, 12.5°C min^{-1} for 8 min, 1°C min^{-1} to 220°C and held for 5 min. Volumetric flow was electronically maintained at 1.2 ml/min. The injector was maintained at 200°C and the transfer line maintained at 280°C. A β-Dex-120 column (30 m × 0.25 mm × 0.25 µm, Supelco, Bellefonte, PA) was used to obtain efficient separation of enantiomers of α-HCH, *trans*- and *cis*-chlordanes. The following temperature program was used: 90°C for 1 min, 2°C min^{-1} for 55 min and held for 22 min. Electronic flow control maintained the flow at 0.8 ml/min. Methane was used as the ionization gas (40% of total flow) and single ion monitoring of the most abundant ions used for the detection of HCHs (253, 255, 257), heptachlor (264, 266, 268), oxychlordane (350, 352) heptachlor-*exo*-epoxide (390, 392), *trans*- and *cis*-nonachlors (442, 444, 446), *trans*- and *cis*-chlordanes (410, 412, 414). Oxychlordane, *trans*-nonachlor, and heptachlor epoxide were quantified using only two ions each as they eluted relatively close to one another.

2.2.7 Standards

Calibration of target analytes was performed using tetrachloro-*m*-xylene (95%) (ULTRA Scientific, North Kingstown, RI) as the internal standard. Standards were used as received: heptachlor (99.6±4%), *o,p'*-DDE (100±4%), oxychlordane (99.6), *p,p'*-DDT (100±4%), *o,p'*-DDT (99.0%) (Accustandard Inc., New Haven, CT), *cis*-chlordane (99.6%), *trans*-chlordane (99.7%), *o,p'*-DDD (97.6%), *cis*-nonachlor (99.5%), *trans*-nonachlor (99.4%) (Supelco, Bellefonte, PA), β-HCH (99.5%) (Chem Service, West Chester PA) *p,p'*-DDE (99.6%), heptachlor-*exo*-epoxide (98.9%), α-HCH (98.7%), *p,p'*-DDD (98.9%) (Sigma-Aldrich, Oakville, ON), $^{13}C_6$ δ-HCH (98%) (Cambridge Isotope Laboratories Inc., Andover MA).

All chromatograms were converted to ASCII format and fitted using PeakFit™ (Version 4, AISN Software Inc., San Jose, CA). Target analytes were fitted using total ions obtained through SIM, $^{13}C_6$ δ-HCH was fitted using m/z 261.

2.2.8 Quality Control

Limits of detection were determined as three times the standard deviation of the noise (Skoog *et al.* 1998).

Table 2.2: Limits of detection (LOD) and quantification (LOQ) of detected target analytes.
Values are expressed as detectable mass in vial.

	LOD	LOQ
α-HCH	0.026 ng	0.0901 ng
β-HCH	0.026 ng	0.0901 ng
γ-HCH	0.026 ng	0.0901 ng
trans-chlordane	0.0242 ng	0.0732 ng
cis-chlordane	0.0242 ng	0.0732 ng
oxychlordane	0.0908 ng	0.227 ng
cis-nonachlor	0.0112 ng	0.0444 ng
trans-nonachlor	0.0112 ng	0.0444 ng
heptachlor-*exo*-epoxide	0.263 ng	0.525 ng
heptachlor	0.092 ng	0.184 ng
p,p'-DDE	0.039 ng	0.13 ng

Quality control was monitored using standard reference materials CRM EC-5 (sediment) and SRM 1945 (organics in whale blubber). Surrogate recoveries for CRM EC-5 varied; for fraction one 51±15% and fraction two 103±46%. All CRM EC-5 concentration values were recovery corrected, using the appropriate recovery standard (Table 2.3). Enantiomer fractions of *trans*-chlordane and *cis*-chlordane compared well to values obtained by Wong *et al.* (2002a) although α-HCH varied by 24%. Recoveries of SRM 1945 could not be accurately determined due to absent recovery standard; however, PCB analysis of SRM 1945 extracts showed good agreement with literature values (Morrissey 2007). Enantiomer fractions for SRM 1945 compare well to those reported by Wong *et al.* (2002a), except heptachlor was not detected (Table 2.3). *trans*-Chlordane and *cis*-chlordane EFs deviated from the values reported by Wong *et al.*, by 3% and 5%

respectively. Additionally, heptachlor-*exo*-epoxide failed to be detected using this method.

Table 2.3: EFs and concentrations (mean±s.d. ng/g wet weight) of detected organochlorines in CRM EC-5 and SRM 1945. Values in parentheses represent individual extract concentrations.

	CRM EC-5		CRM EC-5 (Wong *et al.* 2002)		SRM 1945	SRM 1945 (Wong *et al.* 2002)	
	EF	ng/g wet weight	EF	ng/g wet weight	EF	EF	ng/g wet weight
α-HCH	0.335± 0.027	0.097±0.005	0.446± 0.005	0.16±0.06	0.581± 0.004	0.574± 0.007	16±3
γ-HCH	N/A	(0.089, 0.092)	N/A	N/A	N/A	N/A	N/A
β-HCH	N/A	(0.316)	N/A	N/A	N/A	N/A	N/A
trans-nonachlor	N/A	(3.08)	N/A	N/A	N/A	N/A	N/A
cis-nonachlor	N/A	(0.635, 0.767)	N/A	N/A	N/A	N/A	N/A
trans-chlordane	0.500± 0.002	3.86±1.31	0.497± 0.002	9.1±6.0	0.856± 0.005	0.828± 0.005	13±1
cis-chlordane	0.500± 0.003	3.06±1.06	0.489± 0.003	3.5±1.2	0.181± <0.001	0.172± 0.002	47±3
oxy-chlordane	ND	ND	ND	0.32±0.23	0.621± 0.012	0.625± 0.007	20±2
heptachlor	ND	ND	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	ND	ND	ND	0.03±0.01	N/A	0.622± 0.004	11±1

2.2.9 Statistical Analysis

Racemic enantiomer fractions were calculated based on standards injected throughout the analysis period. Heptachlor-*exo*-epoxide and α-HCH EFs were normally distributed (Kolmogorov-Smirnov α=0.05). Thus, the arithmetic mean and 95% confidence intervals were used to determine if sample EFs were significantly different from racemic values. The geometric mean and corresponding 95% confidence intervals were used for oxychlordane and *trans*- and *cis*-chlordane as the data were not normally distributed. The results of the determination are presented in Table 2.4.

Table 2.4: Determination of racemic EFs and corresponding 95% confidence intervals

	α-HCH N=58	heptachlor epoxide N=14	oxychlordane N=40	*trans*-chlordane N=55	*cis*-chlordane N=54
Arithmetic Mean	0.498	0.503			
Geometric Mean			0.502	0.499	0.501
Lower 95%	0.495	0.494	0.497	0.496	0.497
Upper 95%	0.501	0.513	0.507	0.502	0.505

Statistical analysis was performed using GraphPad Prism (Version 4, GraphPad Software Inc. San Diego, CA). The limited number of data points available for analysis, due mainly to a high proportion of non-detects (NDs), do not allow parametric tests be used for the evaluation of data. To account for the presence of NDs in the datasets, values of half the LOD were substituted for NDs when NDs describe less than half of the samples, and the median was used to represent the data set. A geometric mean gives a value closer to that of the median and removes the effects of outlying values. For dataset containing a majority of NDs the range and median are expressed. When enantiomers are present the concentration is the sum of the individual chromatographic peaks.

2.3 Results and Discussion

2.3.1 Food Web Structure

Stable isotope data for Lac La Biche is presented in Figure 2.1.

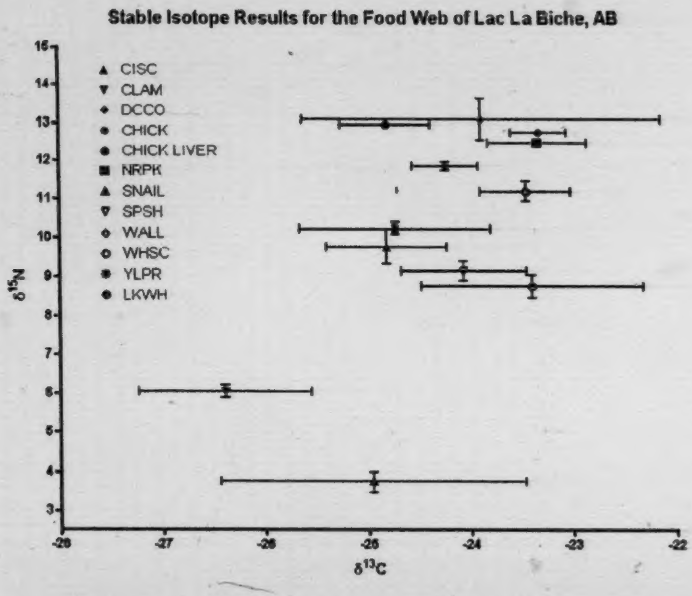

Figure 2.1: Stable isotope analysis of Lac La Biche food web (Earle 2006) Error bars represent one standard deviation: CISC (cisco); DCCO (double-crested cormorant); NRPK (northern pike); SPSH (spottail shiner); WALL (walleye); WHSC (white sucker); YLPR (yellow perch); LKWH (lake whitefish).

No significant difference in the $\delta^{13}C$ of fishes were detected (one-way ANOVA, Tukey's multiple comparison test, 95% CI). These observations indicate that fishes were obtaining carbon from the same source. Similar analysis of $\delta^{15}N$ gives two groups, the first containing: cormorants, chick breast, chick liver, lake whitefish, northern pike, and walleye. The second group contains: cisco, lake whitefish, spottail shiner, whitesucker, yellow perch, and lake whitefish. Boli analysis of nesting cormorants on Lac La Biche showed that approximately 97% of identifiable remains were yellow perch, accounting for roughly 70% of boli biomass (Earle 2006), indicating that yellow perch are a major component of the double-crested cormorant diet at Lac La Biche.

2.3.2 Forage Fish

Forage fish include species such as yellow perch (*Perca flavescens*), cisco or lake herring (*Coregonus artedi*), spottail shiner (*Notropis hudsonius*) and white sucker (*Catostomus commersoni*). β-HCH, oxychlordane, heptachlor-*exo*-epoxide, and DDTs (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *o,p'*-DDE) were not detected in any of the forage fishes.

In most cases, forage species rarely had significant levels (>0.1 ng/g) of α- or γ-HCH, the exception being white sucker liver (Figure 2.2-Figure 2.7). The lone white sucker liver is at a similar δ^{15}N value with respect to other forage fish, yet has a higher wet weight concentration.

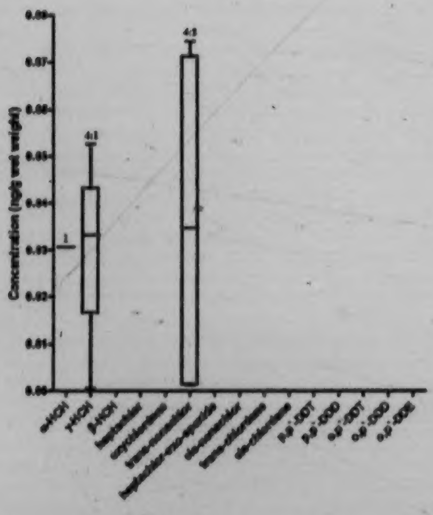

Figure 2.2: Wet weight concentrations detected in cisco from Lac La Biche. Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

Although white sucker otoliths were not analyzed, given the fin length (460mm) it is not unreasonable to assume the age is greater than that of the smaller fishes analysed. It is possible that this white sucker could have been increasing its contaminant body burden for a longer period of time, as it is not uncommon for higher contaminant concentrations to be reported with increasing age (Kidwell *et al.* 1995; Vetter *et al.* 2001). γ-HCH is pervasive throughout forage species. Spottail shiner had concentrations ranging from 0.08 to 0.24 ng/g wet weight (w. w.). Cisco had higher γ-HCH concentrations in liver than in tissue, while yellow perch had lower levels than either spottail shiner or cisco. Unlike cisco liver, yellow perch liver did not appear to have a significantly higher γ-HCH concentration than that of fillet.

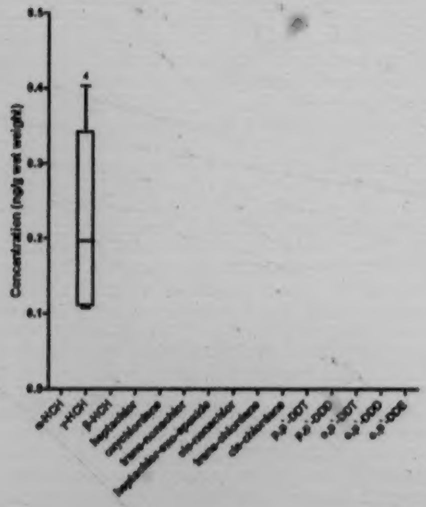

Figure 2.3: Wet weight concentrations detected in cisco livers from Lac La Biche. Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

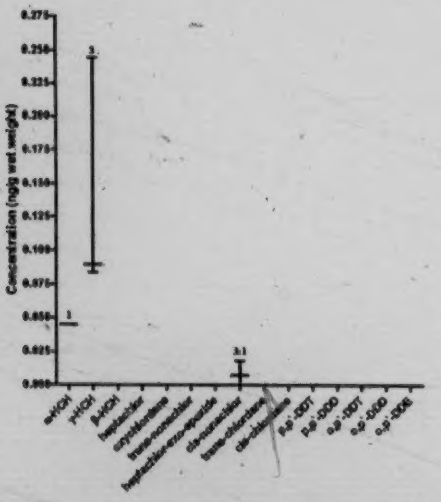

Figure 2.4: Wet weight concentrations detected in spottail shiners from Lac La Biche.

Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

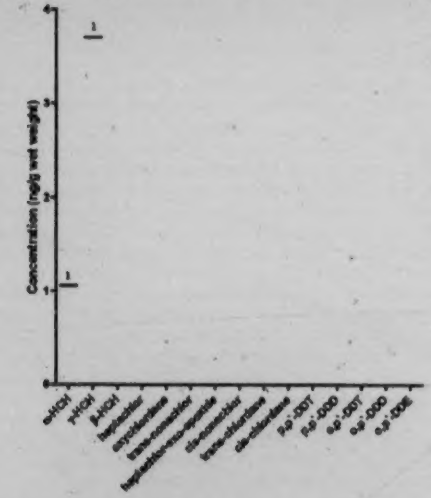

Figure 2.5: Wet weight concentrations detected in white sucker liver from Lac La Biche.

Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

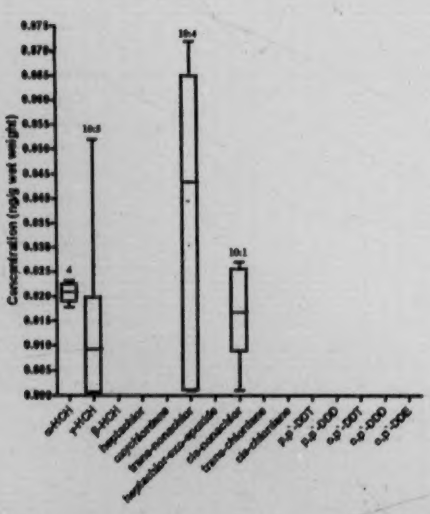

Figure 2.6: Wet weight concentrations detected in yellow perch from Lac La Biche. Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

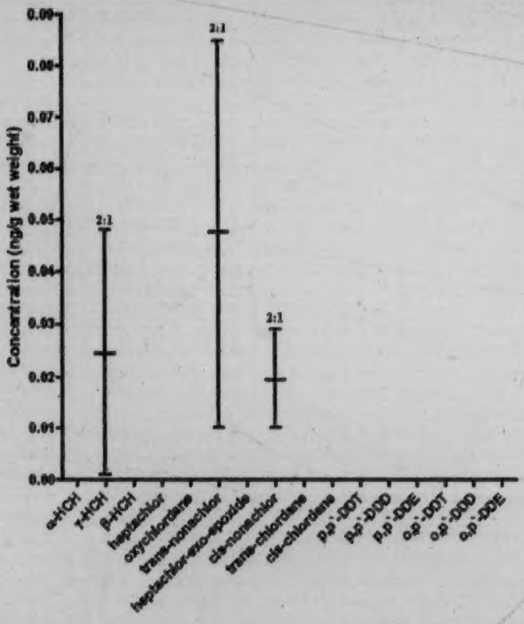

Figure 2.7: Wet weight concentrations detected in yellow perch livers from Lac La Biche.

Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

The range of *trans*-nonachlor in cisco (ND – 0.074 ng/g w. w., N=4), yellow perch (ND – 0.07 ng/g w. w., N=8) do not appear to be significantly different from one another. The one detect of *trans*-nonachlor in yellow perch liver was a composite sample of approximately six fishes, 139.3 ± 22.4 mm and 50.0 ± 24.1 g (mean ± SD). *Cis*-nonachlor was detected in yellow perch (Figure 2.6) and two of three spottail shiner samples (Figure 2.4). A composite sample of snails exhibited a concentration of 0.13 ng/g wet weight. White sucker liver had 1.02 ng/g w. w. of *p,p'*-DDE, while none was detected in the fillet. The *p,p'*-DDE burden in small fishes, spottail shiner, cisco, yellow perch, ranged from ND to 2.51 ng/g w. w. (Figure 2.8). It is worthy to note that *p,p'*-DDE was not detected in yellow perch liver tissues. This may have been an artifact of the instrument detection limit and the relative size and age of the yellow perch. The perch were relatively small and probably young, which makes it quite likely that the perch did not accumulate sufficiently high levels to allow detection. The ΣDDT concentration in yellow perch from Lake Erie (n=20) ranged 0.04 to 0.15 μg/g with 63% being *p,p'*-DDE(Kelso *et al.* 1974).

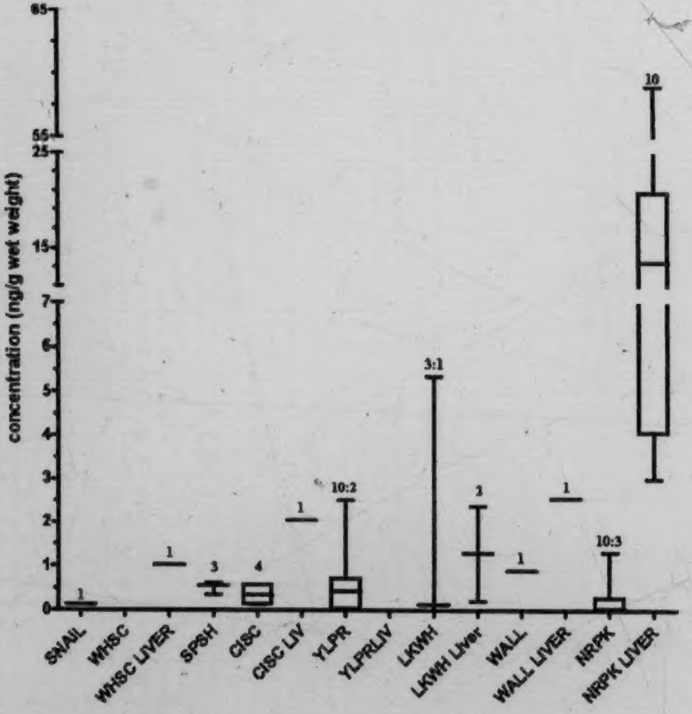

Figure 2.8: Wet weight *p,p'*-DDE concentrations detected throughout the aquatic portion of the Lac La Biche food web. Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank. Y-axis is broken from 7 to 11 and 25 to 55.

2.3.3 Larger Fish

Larger fishes in the Lac La Biche food web include northern pike (*Esox lucius*), walleye (*Stizostedion vitreum*), and lake whitefish (*Coregonus clupeaformis*). Fillets and liver of these species were extracted and analysed separately.

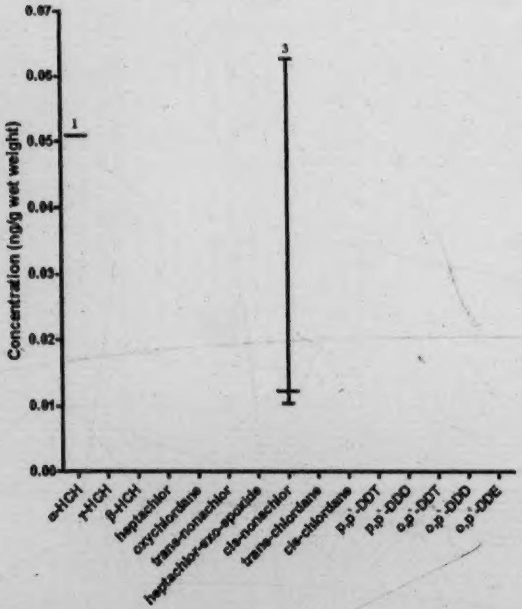

Figure 2.9: Wet weight concentrations detected in northern pike fillets from Lac La Biche.
Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

Northern pike fillet and liver concentrations are presented in Figure 2.9 and Figure 2.10. Comparison of the two tissues shows that contaminants achieve higher concentrations in liver tissue. Kidd *et al.* (1998) sampled northern pike from three lakes throughout the Yukon and detected concentrations of ΣHCH, ΣCHL (*trans*-nonachlor, *cis*-nonachlor, *trans*-chlordane, *cis*-chlordane, and heptachlor epoxide), and ΣDDT ranging from <0.05 to 0.18, 0.05 to 1.42, and 0.16 to 12.3 ng/g w. w. respectively. Northern pike from a eutrophic boreal lake in Sweden, which were only exposed to DDTs through atmospheric deposition, exhibited *p,p'*-DDE concentrations in muscle tissue of 0.13 to 20.9 ng/g fresh weight. (Larsson *et al.* 1992). Given the similar levels of *p,p'*-DDE found in Lac La Biche, northern pike are likely exposed through a similar route of deposition.

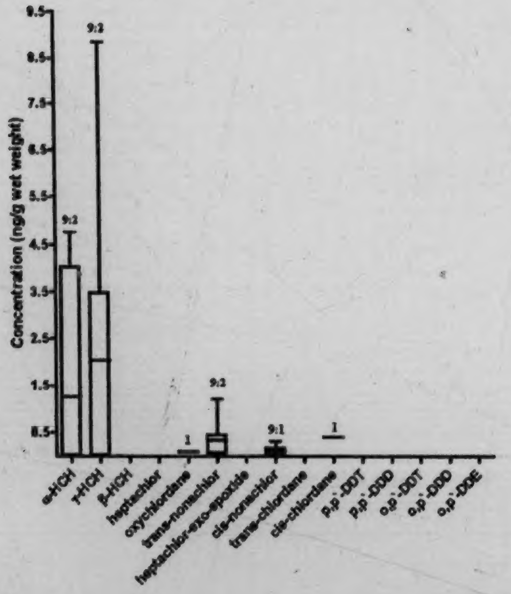

Figure 2.10: Wet weight concentrations detected in northern pike livers from Lac La Biche.
Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

Oxychlordane was detected in single liver and fillet samples of northern pike. The detection of oxychlordane in the lone liver sample was likely due to a greater mass of liver being extracted (12.9 g) compared to other samples (mean = 6.5 g). The fillet was from a northern pike with a 815 mm fin length, which was 73 mm larger than the next. Although the age of the sample was not determined, based on its size it may be older than other pike samples, and therefore may have higher concentrations due to its longevity prior to sampling (Vetter *et al.* 2001).

Contaminant concentrations and EFs detected in walleye tissues are presented in Figure 2.11 and Figure 2.12.

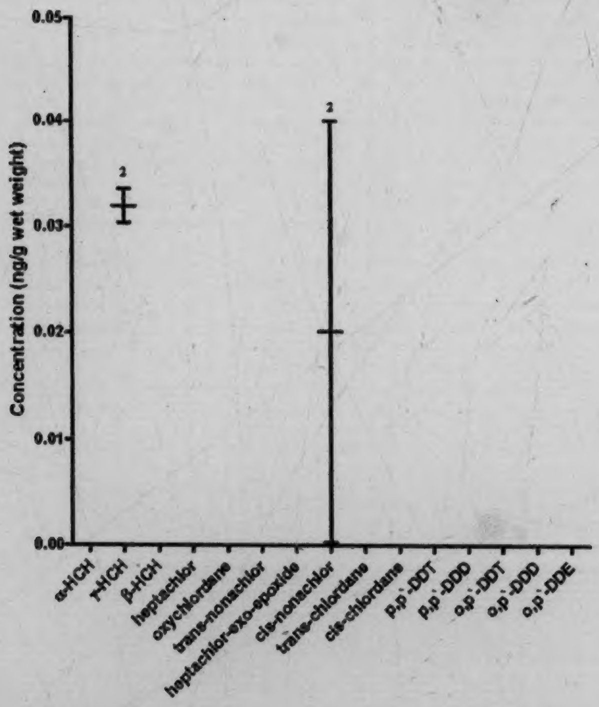

Figure 2.11: Wet weight concentrations detected in walleye fillet from Lac La Biche.
Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

The only compounds detected in walleye tissues were γ-HCH, *trans*-nonachlor, *cis*-nonachlor, *trans*-chlordane, *cis*-chlordane, and *p,p'*-DDE. Walleye taken from Lake Erie, ON by Hickey *et al.* (2006) exhibited 138.1 ng/g w. w. for total DDTs in 1991 and 77.2 ng/g in 1996. Additionally, 109 and 30.6 ng/g w. w. of total chlordanes were detected. Walleye, sampled in 1999 (n=7) and 2000 (n=6), from Lake Erie had non-detectable levels of α-HCH and *p,p'*-DDT (Carlson *et al.* 2006). The minimum mean concentration of *p,p'*-DDE in 2000 was 67±11 ng/g w. w. Mean concentrations of *trans*-nonachlor, *cis*-nonachlor, *trans*-chlordane, and *cis*-chlordane were reported as 7.8±0.8, 6.7±1.2, 5.3±1.0, and 6.7±0.8 ng/g w. w., respectively (Carlson *et al.* 2006). The concentrations detected in walleye from Lac La Biche are much lower than those for walleye obtained from Lake Erie.

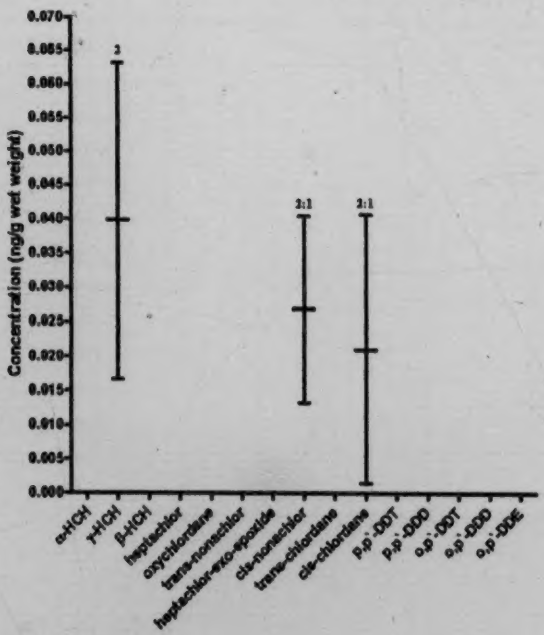

Figure 2.12: Wet weight concentrations detected in walleye livers from Lac La Biche.
Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

Lake whitefish had no detectable residues in fillet. Liver contaminant concentrations are presented in Figure 2.13. The *p,p'*-isomer of DDE was the majority constituent in fillet and liver of lake whitefish; additionally, α- and γ-HCH were both detected in lake whitefish livers. Kidd *et al.* (1998) sampled lake whitefish from lakes throughout the Yukon and detected concentrations of ΣHCH, ΣCHL, and ΣDDT ranging from <0.01 to 5.68, 0.15 to 28.7, and 0.81 to 284 ng/g w. w. respectively. Similarly, lake whitefish liver samples from the St. Lawrence River had 128.2 ng/g w. w. of ΣDDT and 15.4 ng/g w. w. ΣCHL (*trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, and *cis*-nonachlor) (Mikaelian *et al.* 2002). In the Mikaelian *et al.* study α-HCH analysis was not performed and γ-HCH was not detected in any lake whitefish liver samples.

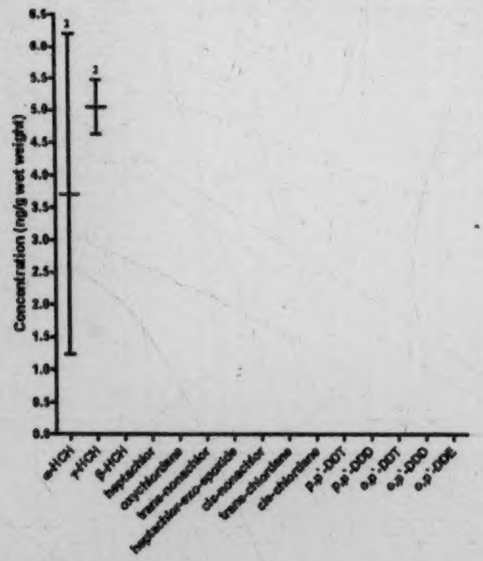

Figure 2.13: Wet weight concentrations detected in lake whitefish liver from Lac La Biche.
Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

Organochlorine concentrations detected in piscivorous fish fillets of Lac La Biche, with the exception of lake whitefish, are lower than those detected by Takazawa *et al.* (2005) in Lake Mashu, Japan. The ranges of HCH concentrations detected in rainbow trout (*Oncorhynchus mykiss*) and kokanee (*Oncorhynchus nerka*) from Lake Mashu, were 0.90 to 2.70, 0.20 to 0.48, and 0.27 to 0.64 ng/g w. w. for α-, β-, and γ-HCH. The average *p,p'*-DDE concentrations were 1.49 and 1.45 ng/g w. w. for male and female trout. Takazawa *et al.* attributed the levels of HCH in Lake Mashu fishes to use of HCH in continental Asia. The isomeric proportion of HCH in Lake Mashu to that of technical HCH is quite similar (Table 2.5).

Table 2.5: Percentage composition of HCH isomers in picivorous fish from Lake Mashu, Japan and in technical HCH (Takazawa *et al.* 2005).

	α-HCH (%)	β-HCH (%)	γ-HCH (%)	δ-HCH (%)
Lake Mashu, JPN	64.6	12.8	21.2	1.4
Technical HCH	65-70	7-10	14-15	~7

2.3.4 Double-crested Cormorants

Wet weight concentrations of adult double-crested cormorant muscle and liver are presented in Figure 2.14, and Figure 2.15. α-HCH was not detected in any adult double-crested cormorant samples. Concentration of ΣHCHs in double-crested cormorant breast tissue from Lac La Biche ranged from ND to 0.186 ng/g wet weight. Cormorants were the only component of the Lac La Biche food web that contained any detectable residues of β-HCH. Cormorants from Lower Therien Lake, AB had detectable levels of β-HCH, 0.065 ppm w. w., in 1969 (Vermeer *et al.* 1970); which is higher than the maximum 0.11 ng/g w. w. detected in this study. γ-HCH was only detected in one double-crested cormorant liver sample, but was detected in 50% of the muscle samples (Table 2.6)

Table 2.6: Wet weight concentration of HCHs in adult double-crested cormorants from Lac La Biche.

Sample	α-HCH (ng/g wet w.)	γ-HCH (ng/g wet w.)	β-HCH (ng/g wet w.)
DCCO 7/18/2006	ND	0.022	ND
DCCO 7/27/2006	ND	0.075	0.111
DCCO 8/21/2006	ND	ND	ND
DCCO 8/21/2006	ND	ND	ND

The wet weight geometric mean of *p,p'*-DDE in double-crested cormorant muscle is 1.99 ng/g, which is below that of 0.95 μg/g, previously reported by Somers *et al.* (1993) for juvenile cormorants.

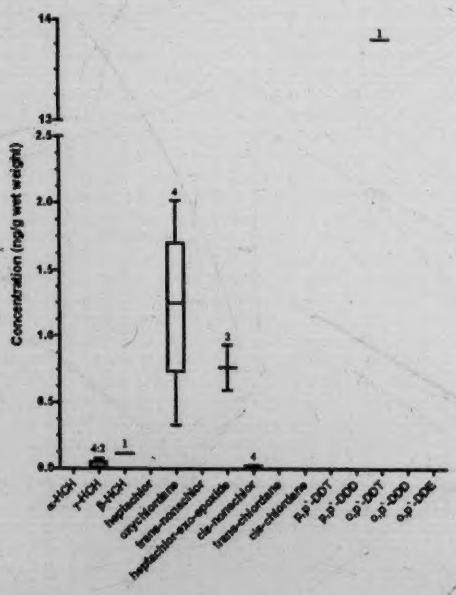

Figure 2.14: Wet weight concentrations detected in adult double-crested cormorants from Lac La Biche.
Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

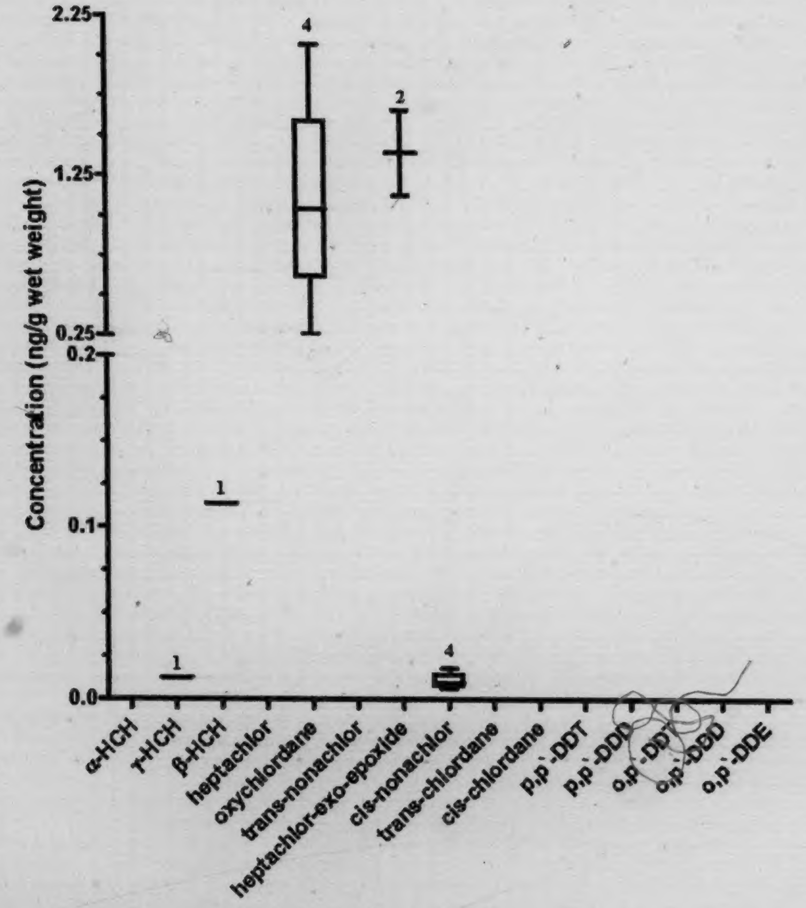

Figure 2.15: Wet weight concentrations detected in adult double-crested cormorant livers from Lac La Biche. Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

2.3.5 Double-crested Cormorant Eggs

Wet weight concentrations of double-crested cormorant eggs are presented in Table 2.7. Median wet weight concentrations detected in cormorant eggs α-, β-, and γ-HCH (0.412, 0.362, and 0.125 ng/g) were lower than those detected during 1968-69 by Vermeer and Reynold (Vermeer *et al.* 1970). Vermeer and Reynolds detected β-BHC (β-HCH) in eggs ranging from ND to 280 ng/g w. w. In 1998 Yamashita *et al.* (1993) detected concentration ranges for α-, β-, and γ-HCH in double-crested cormorant eggs taken from the Great Lakes of 1.7 to 3.5, 3.7 to 7.6, and 1.1 to 2.2 ng/g w. w., respectively. Average concentration of ΣHCHs in double-crested cormorants eggs from the Strait of Georgia, BC were 0.009 ± 0.001 mg/kg w. w. (Harris *et al.* 2005), which is significantly higher than the ΣHCH concentration of 0.902 ng/g determined in this study. The HCH isomeric proportions detected in Strait of Georgia eggs were not reported; although it was stated that α-HCH was the most abundant isomer and γ-HCH was not detected (Harris *et al.* 2005). Adult cormorants from Lac La Biche had no detectable residues of α-HCH. When β-HCH was present it was in excess over γ-HCH, yet γ-HCH was detected more frequently (Table 2.6).

Concentrations of ΣCHLs (*trans*- & *cis*-nonachlors, *trans*- & *cis*-chlordanes, oxychlordane, and heptachlor epoxide) in double-crested cormorant eggs from the Strait of Georgia were 0.17 mg/kg w. w. (Harris *et al.* 2005). *Cis*-chlordane was rarely detected in Strait of Georgia double-crested cormorant eggs (9% in 106 samples) and was not detected in double-crested cormorant eggs from Lac La Biche. The proportional composition of chlordanes in double-crested cormorant eggs analysed in this study (n=3) was: *cis*-chlordane (ND), *trans*-chlordane (ND), *cis*-nonachlor (16%), *trans*-nonachlor (ND), and oxychlordane (84%). Heptachlor-*exo*-epoxide was only detected in one egg sample (11.6 ng/g w. w.) due to an instrument operational error which left heptachlor-*exo*-epoxide undetected in other samples. Composite sampling of double-crested cormorant eggs by Vermeer and Reynolds (Vermeer *et al.* 1970) detected heptachlor-*exo*-

epoxide ranging from 0.015 to 0.075 ppm. Inclusion of heptachlor-*exo*-epoxide in calculating isomeric proportion in the lone double-crested cormorant egg analyzed yielded 8% *cis*-chlordane 37% OXY and 54% heptachlor-*exo*-epoxide. The large proportion of heptachlor-*exo*-epoxide is contrary to that obtained by both Yamashita *et al.* (1993) and Harris *et al.* (2005). Yamashita *et al.* monitored double-crested cormorant eggs from the Great Lakes and detected chlordanes in the following proportions (n=9): *cis*-chlordane (6%), *trans*-chlordane (ND), *cis*-nonachlor (33%), *trans*-nonachlor (9%), and oxychlordane (53%). Harris *et al.*, similar to Yamashita *et al.*, determined that oxychlordane was dominant among all chlordanes in double-crested cormorant eggs from the Strait of Georgia.

Double-crested cormorant eggs from Lac La Biche contained detectable residues of *p,p'*-DDD, *o,p'*-DDT, and majority constituent *p,p'*-DDE (Table 2.7). Somers *et al.* (1993) reported detecting *p,p'*-DDD and/or *p,p'*-DDT in 6% of sampled double-crested cormorant eggs from Alberta; however, the isomer concentrations were not reported. The median concentration, 286 ng/g w. w., of *p,p'*-DDE in double-crested cormorant eggs from Lac La Biche is significantly less than 3.06 µg/g reported by Somers *et al.*, and 1.38 mg/kg w. w. reported by Harris *et al.* The levels of *p,p'*-DDE and *p,p'*-DDD in double-crested cormorant eggs taken from the Great Lakes in 1988 ranged from 2200 to 6300, and 9.4 to 41 ng/g w. w., respectively (Yamashita *et al.* 1993). Which is 2.5 to 7.5 times greater than the highest *p,p'*-DDE residue detected in eggs from Lac La Biche (819 ng/g w. w.). Vermeer and Reynolds (Vermeer *et al.* 1970) reported *p,p'*-DDE concentrations in composite samples of double-crested cormorant eggs, sampled from across the prairies during 1968-69, ranging from 3.43 to 9.00 ppm w. w. Concentrations of *p,p'*-DDE less than 10 μg/g are not considered to be a significant risk to the viability of cormorant eggs (Zitko 1976).

Table 2.7: Summary of wet weight concentrations and enantiomer fractions detected in double-crested cormorant eggs from Lac La Biche

	DCCO Egg N= 3					
	% lipid (median)	**LL**	**UL**	**% lipid (mean)**	**SD**	
	4.49	3.98	5.42	3.98	1.42	
	median (ng/g ww)	**LL**	**UL**	**EF (median)**	**LL**	**UL**
α-HCH	0.412	0.209	1.25	0.58	0.57	0.63
γ-HCH	0.125	ND	0.197			
β-HCH	0.365	ND	0.912			
heptachlor	ND					
oxychlordane	4.97	4.72	8.01	0.71	0.63	0.75
***trans*-nonachlor**	ND					
heptachlor epoxide (N=1)	-	11.6	11.6	-	1.00	1.00
***cis*-nonachlor**	1.38	0.39	1.74			
***trans*-chlordane**	ND					
***cis*-chlordane**	ND					
***p,p'*-DDT**	ND					
***p,p'*-DDD**	0.0161	ND	0.0475			
***p,p'*-DDE**	286	0.284	819			
***o,p'*-DDT**	-	ND	1.71	-	0.61	0.61
***o,p'*-DDD**	ND					
***o,p'*-DDE**	ND					

2.3.6 HCHs in the Lac La Biche Food Web

A positive correlation between α-HCH concentration and $\delta^{15}N$ as observed by Kidd *et al.*(1995) was also observed in this study (Figure 2.16). Bioaccumulation of α-HCH may be occurring in Lac La Biche, whilst γ-HCH does not appear to bioaccumulate. Evidence of γ-HCH elimination from pinfish (*Lagodon rhomboides*) has been observed by Schimmel *et al.* (1977). Schimmel *et al.* found that the BCF for γ-HCH in pinfish was 218, and that subsequent removal to a depuration tank allowed for the elimination of γ-HCH within a week. The relatively high detected levels of γ-HCH in small fishes from Lac La Biche indicate that it is possible for the local region to be a source of γ-HCH.

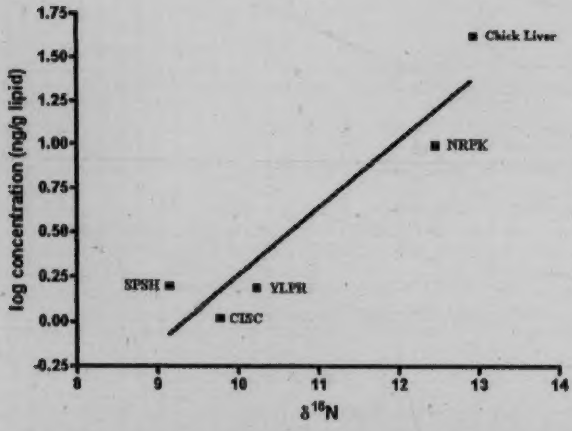

Figure 2.16: Log transformation of highest detected α-HCH concentrations (ng/g lipid) versus δ^{15}nitrogen isotope ratios (‰) in samples from Lac La Biche.

The isomeric signature of HCH in the Lac La Biche food web can be described as being enriched in γ-, and α- isomers, and depleted in the β- isomer. Of the analyzed samples 49% contained quantifiable residues of γ-HCH, whilst 28% and 5% contained α- and β-HCH. It is surprising that β-HCH was not detected in the fishes of the Lac La Biche food web as β-HCH is the isomer most resistant to degradation (Li *et al.* 2002a). The input of β-HCH to the area is probably limited as most of the global transport of β-HCH is due to wet deposition and translocation *via* ocean currents (Li *et al.* 2002a). The ratio of γ-HCH to ΣHCH can be used as a measure of weathering (Li *et al.* 1996), as γ-HCH is currently used in North America while technical HCH is not. Comparison of the ratios of γ-HCH to the sum of γ-HCH and α-HCH within single samples suggests the source of γ-HCH to the Lac La Biche aquatic food web is not technical HCH (Figure 2.17). The percentage of γ-HCH to the sum of γ-HCH and α-HCH based on global usage in 1980 and 1990 was 30% and 29% respectively (Li *et al.* 1996), which is lower than those of Lac La Biche.

The HCH residue proportions in samples from Lac La Biche are dissimilar to that of technical HCH (Figure 2.19), indicating that atmospheric transport, as observed by Takazawa *et al.* (2005), is not a significant source of HCH to the Lac La Biche food web. Takazawa remarked that because of the similarity between the average isomeric signature of HCHs in rainbow trout (*Oncorhynchus mykiss*), kokanee (*Oncorhynchus nerka*), Japanese dace (*Tribolodon ezoe*) from Lake Mashu, Japan to that of technical HCH the detected residues were likely due to atmospheric transport from continental Asia.

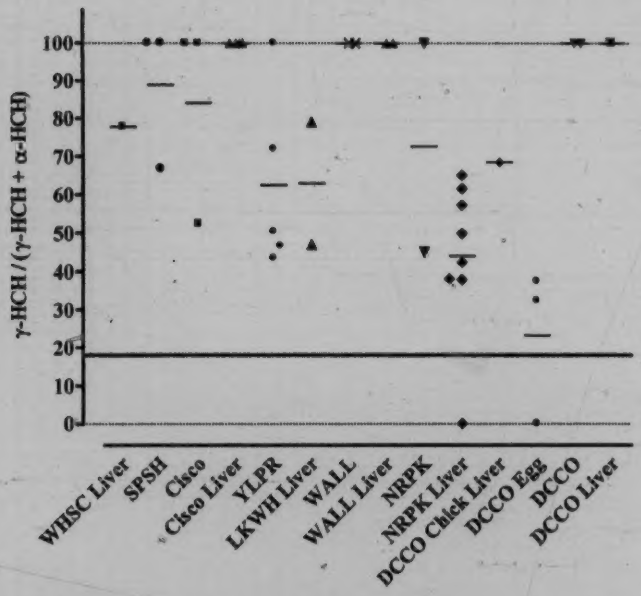

Figure 2.17: Box plot depiction of the percentage of γ-HCH over that of α-HCH in samples from Lac La Biche.
Solid line represents the percentage of γ-HCH in technical HCH (18%). Dotted horizontal lines at 0% and 100% show boundary limits and horizontal line segments denote the mean.

Concentrations γ-HCH detected in Lac La Biche may be due to local inputs as opposed to long range transport. Seasonal trends in γ-HCH concentration in waterways throughout the Canadian Prairie Provinces were observed to be seasonally dependent; increasing from April through June and decreasing into August (Crosley *et al.* 1998). Increased atmospheric loading of γ-HCH has been shown to be temperature dependent (Haugen *et al.* 1998). Comparison of summer temperatures between Lac La Biche, AB in 2004 (54° 46' N, 112° 1' W) to those of a location close to that used by Crosley *et al.*, Artland, SK (52° 46' N, 109° 54' W), shows the mean temperature of Lac La Biche during the summer of 2004 was below that of Artland in 1984, yet not statistically different ($P>0.05$, two-tailed ANOVA, Bartlett's test). It is likely that given current usage γ-HCH may be deposited to the Lac La Biche aquatic food web from regional sources.

The high concentrations of γ-HCH detected in a cormorant chick liver (Figure 2.18) compared to that in adult cormorant liver (Figure 2.15) may be due to the temporal increase in local contamination (Somers *et al.* 1993), as chicks are fed exclusively from the local environment. The low levels of γ-HCH in adult cormorants, compared to northern pike, indicate that cormorants may not receive as much exposure to γ-HCH as northern pike, and/or may have more efficient pathways to eliminate γ-HCH. However, without more detected residues in double-crested cormorant tissues this statement is simply conjecture.

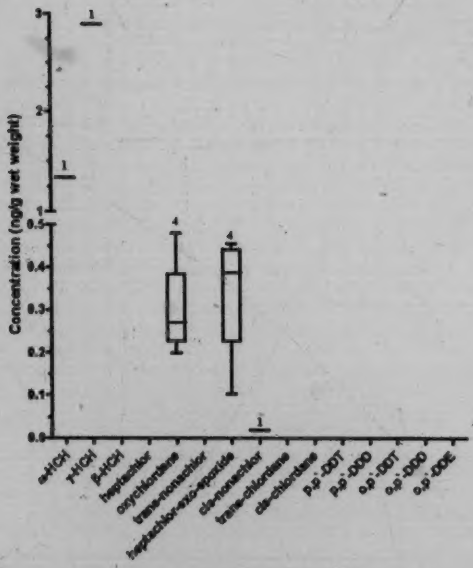

Figure 2.18: Wet weight concentrations detected in double-crested cormorant chick livers from Lac La Biche.
Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

The only samples containing α-, β-, and γ-HCH were double-crested cormorant eggs (section 2.3.5). Isomeric proportions for eggs from Lac La Biche were 27%, 60%, 13% and 30%, 52%, 18% (Figure 2.19). The overall the isomeric proportions of α-, β-, and γ-HCH (n=8) in double-crested cormorant eggs from the Great Lakes were 30%±3, 55%±5, and 15%±3 (Yamashita *et al.* 1993).

Given the similarity between the isomeric signatures of HCHs in double-crested cormorant eggs from Lac La Biche and those observed by Yamashita *et al.*, and the lower concentration present in Lac La Biche, it is likely that the source of double-crested cormorant HCH contamination may be due to their wintering grounds.

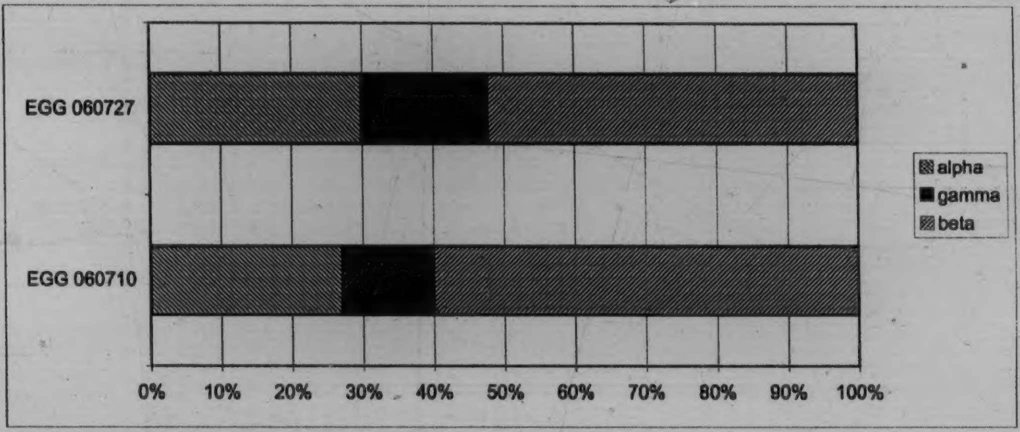

Figure 2.19: Percent composition on HCH in double-crested cormorant eggs sampled from Lac La Biche.

Most α-HCH EFs were less than 0.5 (Figure 2.20), exceptions to this trend were EFs in northern pike liver and cormorant eggs. The EFs in eggs were higher than those of cormorant chick liver. This is surprising for two reasons: The first reason is that residues in adult cormorant were undetected making it impossible to insinuate any maternal transfer. The second reason is that the EF of the chick liver is diametrically opposed to those in the eggs, possibly due to enantioselective biological process during either the formation of the chick or after birth. Kubota et al (Kubota *et al.* 2004) elucidated the dependence of toxicokinetic behaviour of polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) on life-stage, tissue, and concentration in common cormorants (*Phalacrocorax carbo*) from Lake Biwa, Japan. Although these compounds differ in structure to that of α-HCH, the possibility that life-stage could alter a compound's effect in double-crested cormorants cannot be overlooked.

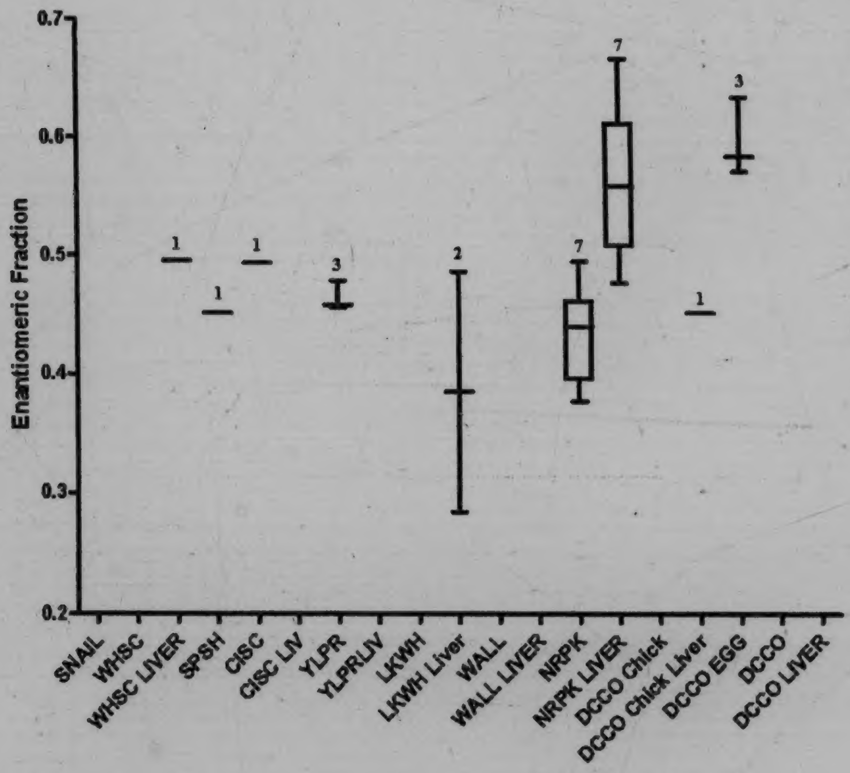

Figure 2.20: Enantiomeric fractions of α-HCH in the Lac La Biche food web.
Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

The EFs of α-HCH in forage species could not be distinguished from racemic as the sample size was insufficient. A one-sample t-test of yellow perch (n=3) suggests that EFs may vary from racemic (i.e., enriched in (-)-α-HCH). Northern pike fillet is enriched in (-)-α-HCH while the livers are enriched in (+)-α-HCH (Figure 2.20). Both tissues are statistically different from racemic, fillet ($p = 0.006$) and liver ($p = 0.054$) (unpaired *t*-test). The differential EFs of α-HCH in northern pike fillet and liver is evidence of enantioselective bioprocessing occurring in northern pike ($p = 0.001$, unpaired *t*-test). To my knowledge divergent EFs between northern pike tissues have not been previously mentioned in the literature. Wong *et al.* (2002b) have determined EFs of *trans*-chlordane in rainbow trout (*Oncorhynchus mykiss*) liver to be significantly non-racemic compared to those in the carcass tissue. Rainbow trout from that study did not show any evidence of enantioselective biotransformation. Dissimilar intra-tissue enantiomeric signatures of α-HCH have been observed in ringed seals (*Phoca hispida*), and polar bears (*Ursus maritimus*) (Wiberg *et al.* 2000). Enantioselective bioprocessing may be occurring in lake whitefish, as α-HCH EFs in livers (N=2) were 0.28 and 0.49. Enantioselective biological processing of pollutants has also been observed in mysids (*Mysis relicta*) (Warner *et al.* 2006) and mummichogs (*Fundulus sp.*) (Vetter *et al.* 2001).

2.3.7 Cyclodienes in the Lac La Biche Food Web

A positive correlation between *trans*-nonachlor and *cis*-nonachlor concentration and $\delta^{15}N$ was also observed in this study (Figure 2.21) and shows that bioaccumulation of these compounds may be occurring. The relative parity between the slopes of *trans*-nonachlor and *cis*-nonachlor in the aquatic portion of the Lac La Biche food web indicates that the accumulation of these isomers is similar. The log concentration versus $\delta^{15}N$ slopes are directly proportional to the lipophilicity of the compound (K_{ow}) (Kidd *et al.* 1998). However, this does not agree with the results obtained for α-HCH (Figure 2.16), as the slope of α-HCH is greater than both *trans*-nonachlor and *cis*-nonachlor while the K_{ow} is lower. The outlying values of *cis*-nonachlor in double-crested cormorant samples is evidence that double-crested cormorants may have more efficient pathways to eliminate *cis*-nonachlor.

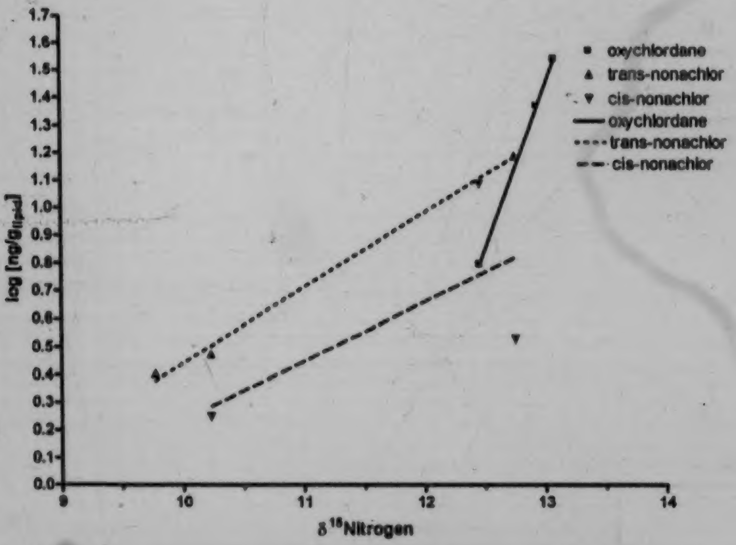

Figure 2.21: log transformed highest-detected lipid concentration (ng/g) versus δ^{15}nitrogen isotope ratios for detected cyclodienes. oxychlordane in double-crested cormorant and northern pike, *trans*-nonachlor in fishes, and *cis*-nonachlor in fishes.

Trans-nonachlor was absent from all double-crested cormorant samples collected from Lac La Biche, contrary to detections of *cis*-nonachlor (Figure 2.14 and Figure 2.15).

The absence of heptachlor in the aquatic portion of the Lac La Biche food web is not surprising. A study in the South Platte River Basin, Colorado only detected heptachlor in sediment and not in any fishes (Tate *et al.* 1996). Heptachlor is usually undetected in fishes as it is quickly biologically transformed to heptachlor-*exo*-epoxide (Schmitt *et al.* 1990). Heptachlor-*exo*-epoxide, compared to heptachlor, was found to be enriched in air samples from North America, with the (+)- enantiomer being most conspicuous (Shen *et* *al.* 2005). The presence of (+)-heptachlor-*exo*-epoxide in double-crested cormorant samples may be due to an enantioselective biological pathway, eliminating heptachlor obtained from food sources in wintering grounds, although a non-racemic source cannot be precluded. Trans-chlordane and *cis*-chlordane were rarely detected in Lac La Biche aquatic samples and this insinuates no significant levels within the food web.

The presence of oxychlordane in adult double-crested cormorants is particularly interesting as the limited detection of *trans*-chlordane and *cis*-chlordane in the Lac La Biche food web suggests that the source of oxychlordane may be from locales other than Lac La Biche. The relative equity between the concentrations in breast tissue and liver of the adult cormorants is interesting, especially when compared to that of the chicks (ND) and chick livers (0.272 ng/g w. w.) which do not show a similar trend (Figure 2.22). Given the small sample size it is difficult it elucidate any sort of growth dependent distribution of oxychlordane. A cormorant egg had significantly higher oxychlordane concentrations than chick livers, double-crested cormorant muscle and liver ($p=0.001$, one-way ANOVA); therefore, it is a possibility that egg laying may be an indirect route of elimination for female cormorants.

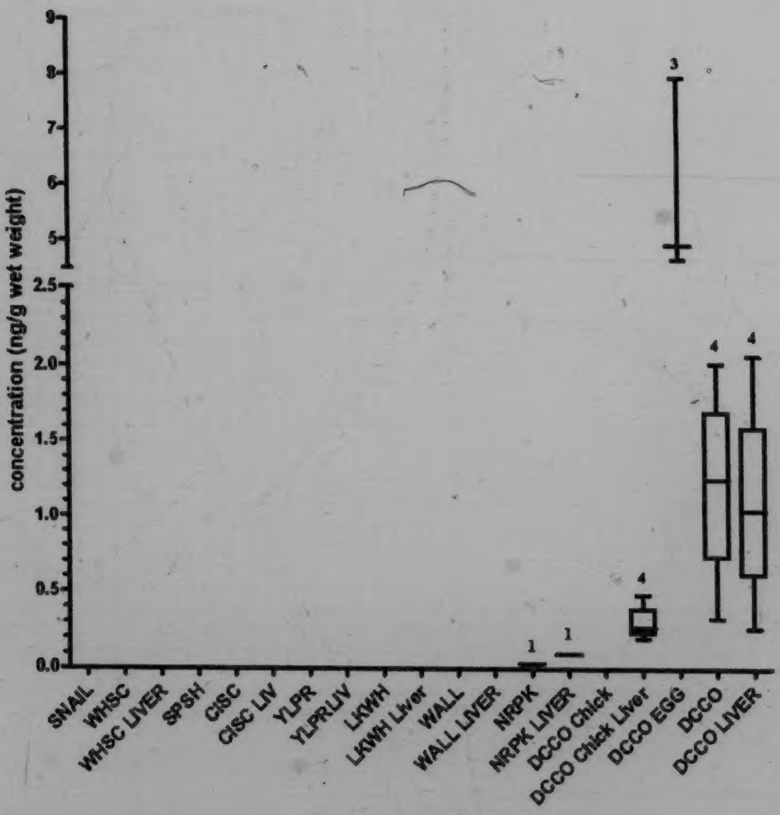

Figure 2.22: Wet weight concentration of oxychlordane in samples from Lac La Biche.
Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot, second number denotes NDs converted to half LOD for statistical purposes. Non-detect samples were left blank.

The EF change of oxychlordane between adult cormorant breast tissue and eggs appears unique, since the EF of the egg has a lower median than that of the both the adult breast tissues and chick liver (Figure 2.23). This may be evidence of enantioselective biological processes. Some of these processes may be: the distribution of the contaminant to the egg, the cormorant's ability to biologically process oxychlordane as it grows, or the production of oxychlordane from chlordanes. The enantioselective elimination of (-)-*trans*-chlordane from rainbow trout was detected by Wong *et al.* (2002b), and Seemamahannop *et al.* (2005) detected the same enantioselective preference in common carp (*Cyprinus carpio*).

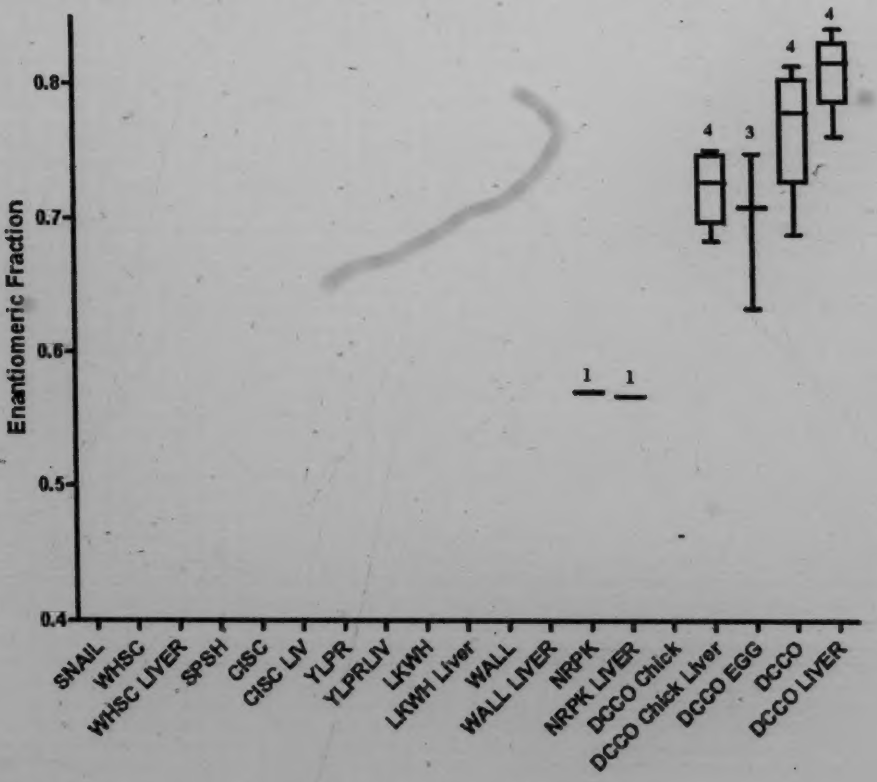

Figure 2.23: EF of oxychlordane in samples from Lac La Biche Bottom and top edges of box represent 25% and 75% percentiles. Whiskers of plot represent range. Horizontal line contained within the box represents the median. N values are placed over the respective sample plot. Non-detect samples were left blank.

2.3.8 DDTs in the Lac La Biche food web

The most pervasive target compound in the analysed samples was *p,p'*-DDE; having been detected in 78% of samples and throughout all species. Plotting the log concentration of *p,p'*-DDE against δ^{15}N (Figure 2.21) illustrates that biomagnification of *p,p'*-DDE is occurring.

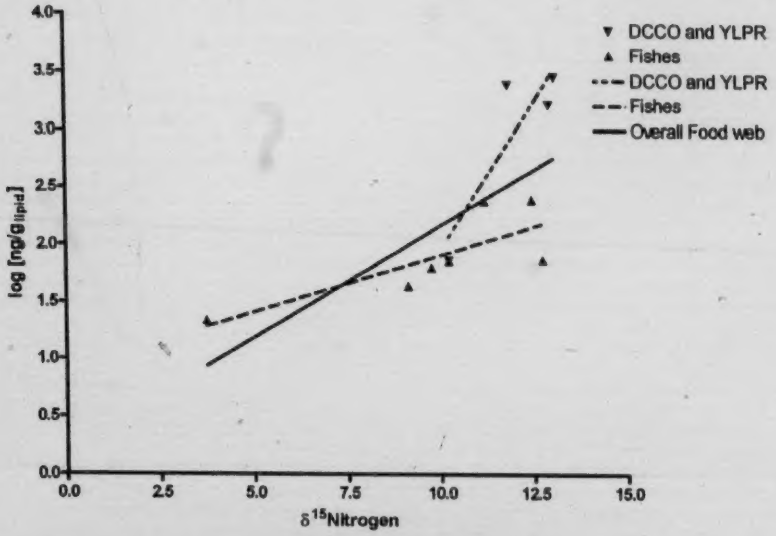

Figure 2.24: Log transformed highest-detected lipid concentration (ng/g) versus δ^{15}nitrogen isotope ratios for *p,p'*-DDE. Groupings consist of double-crested cormorant samples and yellow perch, all fishes, and overall food web.

The calculated biomagnification factor (BMF) of *p,p'*-DDE, based on the lipid normalized median, between yellow perch and cormorant is 70 (Appendix). This value is similar to the value of 73 calculated by Weseloh *et al.* (1983) for yellow perch and double-crested cormorant from Lake Huron. The significant presence of *p,p'*-DDE in the Lac La Biche food web and the absence of most other isomers of DDT, indicates that the lake has not experienced any recent atmospheric deposition of any significance. This is not unexpected as DDT has been banned in Canada since 1972 (Gilkeson *et al.* 2006b).

2.4 Environmental signifigance

The Canadian Council of Ministers of the Environment (CCME) set guidelines for the acceptable levels of contaminants in the environment. These guidelines encompass numeours compartments of the environment such as: air, aquatic life, sediment and soil. Environmental Qualilty Guidelines (2006) for DDE, chlordane, heptachlors in aquatic life were not stated.

Table 2.8: Canadian Council of Ministers of the Environment (CCME) Guidelines. ISQG: interim sediment quality guideline. PEL: probable effect level. EQG: Environmental Quality Guidelines.

	Fresh Water Aquatic Life	Sediment Freshwater		Tissue Residue
		ISQG	PEL	
	(µg/L)	(ng/g)	(ng/g)	(ng/g)
Lindane	0.01	0.94	1.38	-
Heptachlor (Heptachlor epoxide)	No EQG	0.6	2.74	-
Chlordane	No EQG	4.5	8.87	-
DDE	No EQG	1.42	6.75	14

The level of DDE in tissue has been set at 14 ng/g w.w. which is exceeded in some northern pike livers in Lac La Biche. The γ- isomer of HCH has a water concentration of 0.01 µg/L, however this water concentration has probably not been exceeded in Lac La Biche.

2.5 Conclusions

Organochlorine pesticides were detected in the Lac La Biche food web and biomagnification is occurring. γ-HCH is a major pollutant in the fishes of Lac La Biche, and the source of this pollution as likely from local agriculture practices. Adult cormorants appear to have sufficient biological capacity to eliminate γ-HCH and egg laying may be a method of contaminant depuration for female cormorants, specifically for oxychlordane. Heptachlor-*exo*-epoxide and oxychlordane are absent in the aquatic portion of Lac La Biche; although cormorants exhibit particularly high EFs of both these compounds indicating enantioselective biological processes and/or non-racemic sources in wintering grounds. Double-crested cormorants appear to contain completely different organochlorine pollutants compared to other organisms of the food web. Double-crested cormorants appear to be a means of removal for local-source pollutants from Lac La Biche; however, more recalcitrant pollutants (*p,p'*-DDE, *trans*-nonachlor, *cis*-nonachlor, β-HCH, oxychlordane, and heptachlor-*exo*-epoxide) from other locales are brought to Lac La Biche by these same birds.

3 Future Project Directions

Double-crested cormorants are at or near the top of the Lac La Biche food web. As double-crested cormorant population control measures are carried out, a large number of double-crested cormorants will be available for analysis. By focusing on the cormorants it may be possible to determine any enantioselective transfer of heptachlor-*exo*-epoxide or oxychlordane between the chicks and the parents. This would require tissue specific analysis of cormorants, appropriate age and sex determination, and a large sample size spanning eggs, chicks, juveniles, and adult cormorants. Tissues worth analyzing would include: brain, liver, lung, breast, and adipose tissue.

Particularly interesting was the apparent divergence of α-HCH EFs between the fillets and liver tissues of northern pike. A subsequent analysis of northern pike to examine this enantioselective behaviour would need to account for age, sex, size, and sampling date. It would also be recommended to increase the mass of the extractable sample to improve detection. The removal of contaminants from female pike by roe is hypothesized to be a means of slowing the acquisition of pollutant compared to males of the species (Larsson *et al.* 1993).

Also of interest is the effect of γ-HCH on the aquatic portion of the Lac La Biche food web. Although γ-HCH bioaccumulation is not evident, its presence in the food web is likely due to local sources. It may be interesting to determine the seasonally dependent flux of γ-HCH to Lac La Biche, through sampling air, water, and algae. The breadth of such a project would be large; however, a majority of the sampling methods employed would likely be passive and not require the same field time as a food web study.

4 References

The following are acronyms present in the References section.

ATSDR: Agency for Toxic Substances and Disease Registry

BCPC: British Crop Protection Council

EC: Environment Canada

EPA: Environmental Protection Agency

HSDB: Hazardous Substances Data Bank

IARC: International Agency for Research on Cancer

WHO: World Health Organization

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5 Appendix I

The tables contained within Appendix I contain sample specific information including, but not limited to: extracted mass, recoveries, % lipid determination, and lipid-normalized concentrations. Various methods of assigning sample IDs were utilized throughout the course of this study. Initially samples were number (starting at 1) or lettered (started at A) to distinguish them from similar samples. Exceptions to the use of lettered identifiers occur with the addition of sampling location, TB, WB, EB referring to the Town, West, and East basins respectively, or the use of "L" referring to a liver sample. The method of numbering samples was found to be difficult to maintain; therefore, numbers were dropped in favour of using extraction dates ie., 060723 (year month day), or mass or length.

5.1 Cisco

	Species	CISC	CISC	CISC	CISC
	Sample ID	WBCISC1	WBCISC2	215CISC	179CISC
	Date Extracted	7/20/2005	7/20/2005	7/29/2005	7/29/2005
	Fork Length (mm)	241	279	215	179
	Mass Extracted	10.842	9.021	10.763	10.810
	% Lipid	1.95	0.89	4.89	2.93
	Mass Lipid	0.212	0.080	0.526	0.317
	PCB 30 recovery F1	0.491	0.554	N/A	N/A
	PCB 204 recovery F1	0.597	0.617	1.03	1.01
	$^{13}C_6$ δ-HCH BGB-172 F2	N/A	N/A	N/A	N/A
	$^{13}C_6$ δ-HCH β-Dex 120 F2	N/A	N/A	N/A	N/A
α-HCH	Measured Conc (ng)	ND	ND	ND	0.333
	Wet wt (ng/g)	ND	ND	ND	0.031
	Lipid-normalized (ng/g lipid)	ND	ND	ND	1.05
	EF	N/A	N/A	N/A	0.494
γ-HCH	Measured Conc (ng)	ND	0.476	0.349	0.367
	Wet wt (ng/g)	0.001	0.053	0.032	0.034
	Lipid-normalized (ng/g lipid)	0.031	5.941	0.663	1.16
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	WBCISC1	WBCISC2	215CISC	179CISC
heptachlor	**Measured Conc (ng)**	**ND**	**ND**	**ND**	**ND**
	Wet wt (ng/g)	**ND**	**ND**	**ND**	**ND**
	Lipid-normalized (ng/g lipid)	**ND**	**ND**	**ND**	**ND**
	EF	**N/A**	**N/A**	**N/A**	**N/A**
oxychlordane	**Measured Conc (ng)**	**ND**	**ND**	**ND**	**ND**
	Wet wt (ng/g)	**ND**	**ND**	**ND**	**ND**
	Lipid-normalized (ng/g lipid)	**ND**	**ND**	**ND**	**ND**
	EF	**N/A**	**N/A**	**N/A**	**N/A**
trans-nonachlor	**Measured Conc (ng)**	**ND**	**ND**	**0.733**	**0.805**
	Wet wt (ng/g)	**0.001**	**0.001**	**0.068**	**0.074**
	Lipid-normalized (ng/g lipid)	**0.063**	**0.166**	**1.39**	**2.54**
	EF	**N/A**	**N/A**	**N/A**	**N/A**
heptachlor-*exo*-epoxide	**Measured Conc (ng)**	**ND**	**ND**	**ND**	**ND**
	Wet wt (ng/g)	**ND**	**ND**	**ND**	**ND**
	Lipid-normalized (ng/g lipid)	**ND**	**ND**	**ND**	**ND**
	EF	**N/A**	**N/A**	**N/A**	**N/A**
cis-nonachlor	**Measured Conc (ng)**	**ND**	**ND**	**ND**	**ND**
	Wet wt (ng/g)	**ND**	**ND**	**ND**	**ND**
	Lipid-normalized (ng/g lipid)	**ND**	**ND**	**ND**	**ND**
	EF	**N/A**	**N/A**	**N/A**	**N/A**
trans-chlordane	**Measured Conc (ng)**	**ND**	**ND**	**ND**	**ND**
	Wet wt (ng/g)	**ND**	**ND**	**ND**	**ND**
	Lipid-normalized (ng/g lipid)	**ND**	**ND**	**ND**	**ND**
	EF	**N/A**	**N/A**	**N/A**	**N/A**
cis-chlordane	**Measured Conc (ng)**	**ND**	**ND**	**ND**	**ND**
	Wet wt (ng/g)	**ND**	**ND**	**ND**	**ND**
	Lipid-normalized (ng/g lipid)	**ND**	**ND**	**ND**	**ND**
	EF	**N/A**	**N/A**	**N/A**	**N/A**

	Sample ID	WBCISC1	WBCISC2	215CISC	179CISC
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	6.25	5.08	1.27	1.43
	Wet wt (ng/g)	0.576	0.564	0.118	0.132
	Lipid-normalized (ng/g lipid)	29.5	63.5	2.41	4.52
	EF	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.2 Cisco liver

	Species	CISC LIV	CISC LIV	CISC LIV	CISC LIV
	Sample ID	CISCLIV1	CISCLIV2	215CISCL	179CISCL
	Date Extracted	7/20/2005	7/20/2005	7/29/2005	7/29/2005
	Fork Length (mm)	241	279	215	179
	Mass Extracted	0.997	1.870	0.815	0.889
	% Lipid	4.57	5.10	6.75	5.44
	Mass Lipid	0.046	0.095	0.055	0.048
	PCB 30 recovery F1	0.543	N/A	N/A	N/A
	PCB 204 recovery F1	0.631	0.940	0.942	0.925
	$^{13}C_6$ δ-HCH BGB-172 F2	N/A	N/A	N/A	N/A
	$^{13}C_6$ δ-HCH β-Dex 120 F2	N/A	N/A	N/A	N/A
α-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	0.402	0.526	0.088	0.100
	Wet wt (ng/g)	0.403	0.281	0.107	0.112
	Lipid-normalized (ng/g lipid)	8.81	5.51	1.59	2.07
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	CISCLIV1	CISCLIV2	215CISCL	179CISCL
heptachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	CISCLIV1	CISCLIV2	215CISCL	179CISCL
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	2.04	ND	ND	ND
	Wet wt (ng/g)	2.04	ND	ND	ND
	Lipid-normalized (ng/g lipid)	44.6	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.3 Double-crested cormorant

	Species	DCCO	DCCO	DCCO	DCCO
	Sample ID	DCCO060718	DCCO060727	OCT SIA-127 DCCO B TISSUE	OCT SIA 2481 DCCO A TISSUE
	Date Extracted	7/18/2006	7/27/2006	8/21/2006	8/21/2006
	Fork Length (mm)	10/1/2004	Oct	0	0
	Mass Extracted	9.747	6.119	8.906	8.389
	% Lipid	6.72	7.22	3.95	7.18
	Mass Lipid	0.655	0.442	0.352	0.602
	PCB 30 recovery F1	0.260	0.529	0.885	0.264
	PCB 204 recovery F1	1.35	1.23	0.632	0.990
	$^{13}C_6$ δ-HCH BGB-172 F2	0.552	0.672	0.320	0.482
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.988	0.869	0.329	0.472
α-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	0.218	0.459	ND	ND
	Wet wt (ng/g)	0.022	0.075	0.001	0.001
	Lipid-normalized (ng/g lipid)	0.333	1.04	0.019	0.011
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	0.679	ND	ND
	Wet wt (ng/g)	ND	0.111	ND	ND
	Lipid-normalized (ng/g lipid)	ND	1.54	ND	ND
	EF	N/A	N/A	N/A	N/A

Sample ID		DCCO060718	DCCO060727	OCT SIA-127 DCCO B TISSUE	OCT SIA 2481 DCCO A TISSUE
heptachlor	**Measured Conc (ng)**	**ND**	**ND**	**ND**	**ND**
	Wet wt (ng/g)	**ND**	**ND**	**ND**	**ND**
	Lipid-normalized (ng/g lipid)	**ND**	**ND**	**ND**	**ND**
	EF	**N/A**	**N/A**	**N/A**	**N/A**
oxychlordane	Measured Conc (ng)	3.22	6.89	12.3	17.0
	Wet wt (ng/g)	0.330	1.13	1.38	2.02
	Lipid-normalized (ng/g lipid)	4.92	15.6	34.8	28.1
	EF	0.689	0.795	0.815	0.765
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	8.34	4.97
	Wet wt (ng/g)	ND	ND	0.936	0.592
	Lipid-normalized (ng/g lipid)	N/A	N/A	23.7	8.25
	EF	N/A	N/A	1.00	1.00
cis-nonachlor	Measured Conc (ng)	0.236	0.141	0.274	0.215
	Wet wt (ng/g)	0.024	0.023	0.031	0.026
	Lipid-normalized (ng/g lipid)	0.361	0.318	0.778	0.357
	EF	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	DCCO060718	DCCO060727	OCT SIA-127 DCCO B TISSUE	OCT SIA 2481 DCCO A TISSUE
p,p′-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p′-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p′-DDE	Measured Conc (ng)	2.26	ND	1.03E+03	1.52E+03
	Wet wt (ng/g)	0.232	0.003	116	181
	Lipid-normalized (ng/g lipid)	3.46	0.044	2.94E+03	2.52E+03
	EF	N/A	N/A	N/A	N/A
o,p′-DDT	Measured Conc (ng)	ND	84.5	ND	ND
	Wet wt (ng/g)	ND	13.8	ND	ND
	Lipid-normalized (ng/g lipid)	ND	191	ND	ND
	EF	N/A	0.605	N/A	N/A
o,p′-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p′-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.4 Double-crested cormorant chick

	Species	DCCO Chick	DCCO Chick	DCCO Chick
	Sample ID	DCCO CHICK	DCCO 1472 TISSUE	DCCO 637 CHICK
	Date Extracted	6/14/2006	8/21/2006	8/21/2006
	Mass	708 g	1472 g	637 g
	Mass Extracted	4.335	8.316	6.819
	% Lipid	2.23	1.84	2.36
	Mass Lipid	0.096	0.153	0.161
	PCB 30 recovery F1	0.334	0.272	0.788
	PCB 204 recovery F1	0.928	0.972	1.019
	$^{13}C_6$ δ-HCH BGB-172 F2	1.90	0.400	0.438
	$^{13}C_6$ δ-HCH β-Dex 120 F2	2.16	0.446	0.405
α-HCH	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	0.306	ND
	Wet wt (ng/g)	ND	0.037	ND
	Lipid-normalized (ng/g lipid)	ND	2.00	ND
	EF	N/A	N/A	N/A

	Sample ID	DCCO CHICK	DCCO 1472 TISSUE	DCCO 637 CHICK
heptachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A

	Sample ID	DCCO CHICK	DCCO 1472 TISSUE	DCCO 637 CHICK
p,p'-DDT	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	241	264	169
	Wet wt (ng/g)	55.7	31.7	24.7
	Lipid-normalized (ng/g lipid)	2.50E+03	1.73E+03	1.05E+03
	EF	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A

5.5 Double-crested cormorant chick liver

	Species	DCCO Chick Liver	DCCO Chick Liver	DCCO Chick Liver	DCCO Chick Liver
	Sample ID	CHICKLIV	DCCO 1111.4 LIVER	DCCO 637 LIVER	DCCO 1472 LIVER
	Date Extracted	6/14/2006	8/3/2006	8/3/2006	8/21/2006
	Mass	708 g	1111 g	637 g	1472 g
	Mass Extracted	6.096	5.870	5.424	9.371
	% Lipid	3.15	2.04	3.82	4.87
	Mass Lipid	0.192	0.120	0.207	0.457
	PCB 30 recovery F1	0.073	0.260	0.094	N/A
	PCB 204 recovery F1	0.923	1.34	1.34	0.92
	$^{13}C_6$ δ-HCH BGB-172 F2	1.89	0.779	0.616	0.394
	$^{13}C_6$ δ-HCH β-Dex 120 F2	2.08	0.658	0.688	0.350
α-HCH	Measured Conc (ng)	8.16	ND	ND	ND
	Wet wt (ng/g)	1.34	ND	ND	ND
	Lipid-normalized (ng/g lipid)	42.5	ND	ND	ND
	EF	0.452	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	17.7	ND	ND	ND
	Wet wt (ng/g)	2.90	ND	ND	ND
	Lipid-normalized (ng/g lipid)	92.2	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	CHICKLIV	DCCO 1111.4 LIVER	DCCO 637.5 LIVER	DCCO 1472 LIVER
heptachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	1.21	2.82	1.58	2.37
	Wet wt (ng/g)	0.199	0.481	0.290	0.253
	Lipid-normalized (ng/g lipid)	6.33	23.6	7.61	5.20
	EF	0.710	0.751	0.744	0.684
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	0.629	2.68	1.90	4.01
	Wet wt (ng/g)	0.103	0.457	0.350	0.428
	Lipid-normalized (ng/g lipid)	3.28	22.4	9.17	8.79
	EF	1.00	0.956	0.923	1.00
cis-nonachlor	Measured Conc (ng)	ND	ND	ND	0.181
	Wet wt (ng/g)	ND	ND	ND	0.019
	Lipid-normalized (ng/g lipid)	ND	ND	ND	0.396
	EF	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	CHICKLIV	DCCO 1111.4 LIVER	DCCO 637.5 LIVER	DCCO 1472 LIVER
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	65.3	203	187	134
	Wet wt (ng/g)	10.7	34.5	34.5	14.3
	Lipid-normalized (ng/g lipid)	341	1.69E+03	904	293
	EF	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.6 Double-crested cormorant eggs

	Species	DCCO EGG	DCCO EGG	DCCO EGG
	Sample ID	EGG 060519	EGG 060710	EGG 060727
	Date Extracted	5/19/2006	7/10/2006	7/27/2006
	Fork Length (mm)	43.5 g	44.5 g	50.6 g
	Mass Extracted	42.529	43.221	49.566
	% Lipid	4.49	5.42	3.98
	Mass Lipid	1.908	2.343	1.971
	PCB 30 recovery F1	0.865	0.249	0.180
	PCB 204 recovery F1	3.73	2.13	1.74
	$^{13}C_6$ δ-HCH BGB-172 F2	0.558	0.366	0.723
	$^{13}C_6$ δ-HCH β-Dex 120 F2	5.74	0.231	0.759
α-HCH	Measured Conc (ng)	53.2	17.8	10.4
	Wet wt (ng/g)	1.25	0.412	0.209
	Lipid-normalized (ng/g lipid)	27.9	7.60	5.26
	EF	0.585	0.635	0.572
γ-HCH	Measured Conc (ng)	ND	8.53	6.20
	Wet wt (ng/g)	0.000	0.197	0.125
	Lipid-normalized (ng/g lipid)	0.003	3.64	3.14
	EF	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	39.4	18.1
	Wet wt (ng/g)	0.000	0.912	0.365
	Lipid-normalized (ng/g lipid)	0.003	16.8	9.19
	EF	N/A	N/A	N/A

	Sample ID	EGG 060519	EGG 060710	EGG 060727
heptachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	340.6	203.8	246.2
	Wet wt (ng/g)	8.01	4.72	4.97
	Lipid-normalized (ng/g lipid)	178.5	87.0	124.9
	EF	0.749	0.709	0.634
trans-nonachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	494.5	ND	ND
	Wet wt (ng/g)	11.6	ND	ND
	Lipid-normalized (ng/g lipid)	259.1	N/A	N/A
	EF	1.00	N/A	N/A
cis-nonachlor	Measured Conc (ng)	74.1	16.8	68.6
	Wet wt (ng/g)	1.74	0.388	1.38
	Lipid-normalized (ng/g lipid)	38.8	7.17	34.8
	EF	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A

	Sample ID	EGG 060519	EGG 060710	EGG 060727
p,p′-DDT	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
p,p′-DDD	Measured Conc (ng)	0.684	ND	2.35
	Wet wt (ng/g)	0.016	0.000	0.047
	Lipid-normalized (ng/g lipid)	0.358	0.008	1.19
	EF	N/A	N/A	N/A
p,p′-DDE	Measured Conc (ng)	3.48E+04	12.3	1.42E+04
	Wet wt (ng/g)	819.4	0.284	286.2
	Lipid-normalized (ng/g lipid)	1.83E+04	5.24	7.20E+03
	EF	N/A	N/A	N/A
o,p′-DDT	Measured Conc (ng)	ND	ND	84.5
	Wet wt (ng/g)	ND	ND	1.71
	Lipid-normalized (ng/g lipid)	ND	ND	42.9
	EF	N/A	N/A	0.605
o,p′-DDD	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
o,p′-DDE	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A

5.7 Double-crested cormorant liver

	Species	DCCO LIVER	DCCO LIVER	DCCO LIVER	DCCO LIVER
	Sample ID	DCCOLIV060718	DCCOLIV060727	OCT SIA-127 DCCO B LIVER	OCT SIA 2481 DCCO A LIVER
	Date Extracted	7/18/2006	7/27/2006	8/21/2006	8/21/2006
	Fork Length (mm)		Oct		
	Mass Extracted	7.811	5.088	8.376	10.244
	% Lipid	3.17	5.67	5.26	4.29
	Mass Lipid	0.247	0.288	0.440	0.439
	PCB 30 recovery F1	0.542	0.362	0.339	0.493
	PCB 204 recovery F1	1.06	0.801	0.745	0.733
	$^{13}C_6$ δ-HCH BGB-172 F2	0.647	0.763	0.399	0.482
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.603	0.927	0.462	0.472
α-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	0.099	ND	ND	ND
	Wet wt (ng/g)	0.013	ND	ND	ND
	Lipid-normalized (ng/g lipid)	0.399	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	0.580	ND	ND
	Wet wt (ng/g)	ND	0.114	ND	ND
	Lipid-normalized (ng/g lipid)	ND	2.01	ND	ND
	EF	N/A	N/A	N/A	N/A

Sample ID		DCCOLIV060718	DCCOLIV060727	OCT SIA-127 DCCO B LIVER	OCT SIA 2481 DCCO A LIVER
heptachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	2.05	4.92	9.35	21.2
	Wet wt (ng/g)	0.262	0.968	1.12	2.07
	Lipid-normalized (ng/g lipid)	8.28	17.1	21.2	48.3
	EF	0.762	0.823	0.843	0.812
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	9.45	17.0
	Wet wt (ng/g)	ND	ND	1.13	1.66
	Lipid-normalized (ng/g lipid)	N/A	N/A	21.5	38.6
	EF	N/A	N/A	1.00	1.00
cis-nonachlor	Measured Conc (ng)	0.050	0.092	0.077	0.106
	Wet wt (ng/g)	0.006	0.018	0.009	0.010
	Lipid-normalized (ng/g lipid)	0.204	0.321	0.175	0.241
	EF	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	DCCOLIV060718	DCCOLIV060727	OCT SIA-127 DCCO B LIVER	OCT SIA 2481 DCCO A LIVER
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	0.898	ND	335	961
	Wet wt (ng/g)	0.115	0.004	40.0	93.9
	Lipid-normalized (ng/g lipid)	3.63	0.068	762	2.19E+03
	EF	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.8 Lake whitefish

	Species	LKWH	LKWH	LKWH
	Sample ID	LKWH 434 A	LKWH 446 B	LKWH 492 C
	Date Extracted	2/8/2006	2/8/2006	2/8/2006
	Fork Length (mm)	434	446	492
	Mass Extracted	11.485	9.355	9.659
	% Lipid	1.90	1.38	2.21
	Mass Lipid	0.218	0.129	0.214
	PCB 30 recovery F1	0.086	0.121	0.048
	PCB 204 recovery F1	0.778	0.699	0.738
	$^{13}C_6$ δ-HCH BGB-172 F2	0.554	N/A	N/A
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.655	N/A	0.675
α-HCH	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A

	Sample ID	LKWH 434 A	LKWH 446 B	LKWH 492 C
heptachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A

	Sample ID	LKWH 434 A	LKWH 446 B	LKWH 492 C
p,p'-DDT	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	ND	1.18	51.8
	Wet wt (ng/g)	0.002	0.127	5.36
	Lipid-normalized (ng/g lipid)	0.089	9.18	243
	EF	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND
	EF	N/A	N/A	N/A

5.9 Lake whitefish liver

	Species	LKWH Liver	LKWH Liver
	Sample ID	LKWH434L	LKWH492L
	Date Extracted	6/14/2006	6/14/2006
	Fork Length (mm)	434	492
	Mass Extracted	6.673	9.975
	% Lipid	3.91	14.7
	Mass Lipid	0.261	1.46
	PCB 30 recovery F1	0.187	0.362
	PCB 204 recovery F1	0.863	0.863
	$^{13}C_6$ δ-HCH BGB-172 F2	1.99	1.29
	$^{13}C_6$ δ-HCH β-Dex 120 F2	2.18	0.967
α-HCH	Measured Conc (ng)	8.23	61.8
	Wet wt (ng/g)	1.23	6.20
	Lipid-normalized (ng/g lipid)	31.6	42.3
	EF	0.284	0.487
γ-HCH	Measured Conc (ng)	30.9	54.6
	Wet wt (ng/g)	4.63	5.48
	Lipid-normalized (ng/g lipid)	118	37.4
	EF	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A

	Sample ID	LKWH434L	LKWH492L
heptachlor	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A

	Sample ID	LKWH434L	LKWH492L
p,p'-DDT	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
p,p'-DDE	Measured Conc (ng)	1.38	23.7
	Wet wt (ng/g)	0.208	2.37
	Lipid-normalized (ng/g lipid)	5.31	16.2
	EF	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND
	Wet wt (ng/g)	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND
	EF	N/A	N/A

5.10 Northern pike

	Species	NRPK	NRPK	NRPK	NRPK	NRPK
	Sample ID	NRPK 615	NRPK 614	NRPK 612	NRPK 598	NRPK 584
	Date Extracted	10/19/2005	2/24/2006	2/24/2006	2/24/2006	2/24/2006
	Fork Length (mm)	615	614	612	598	584
	Mass Extracted	5.373	9.497	8.964	8.802	8.510
	% Lipid	0.52	0.64	0.50	0.80	0.45
	Mass Lipid	0.028	0.061	0.045	0.070	0.038
	PCB 30 recovery F1	0.539	0.168	0.235	0.315	N/A
	PCB 204 recovery F1	N/A	0.707	0.728	0.775	0.678
	$^{13}C_6$ δ-HCH BGB-172 F2	14.0	0.201	0.324	0.665	0.750
	$^{13}C_6$ δ-HCH β-Dex 120 F2	N/A	0.254	0.319	0.508	0.542
α-HCH	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	ND	nd	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

Sample ID		NRPK 615	NRPK 614	NRPK 612	NRPK 598	NRPK 584
heptachlor	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	ND	ND	0.109	ND
	Wet wt (ng/g)	ND	ND	ND	0.012	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	1.55	ND
	EF	N/A	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

	Sample ID	NRPK 615	NRPK 614	NRPK 612	NRPK 598	NRPK 584
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	7.07	1.81	ND	ND	0.298
	Wet wt (ng/g)	1.32	0.190	0.002	0.002	0.035
	Lipid-normalized (ng/g lipid)	251	29.6	0.434	0.277	7.83
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

5.11 Northern pike

	Species	NRPK	NRPK	NRPK	NRPK	NRPK
	Sample ID	660 NRPK	675 NRPK	NRPK 620	NRPK 815	NRPK 638
	Date Extracted	5/15/2006	5/15/2006	7/10/2006	7/10/2006	8/3/2006
	Fork Length (mm)	660	675	620	815	638
	Mass Extracted	5.862	5.405	24.425	19.352	4.818
	% Lipid	0.56	0.78	0.91	0.51	0.86
	Mass Lipid	0.033	0.042	0.222	0.099	0.041
	PCB 30 recovery F1	0.595	0.526	0.193	0.192	3.243
	PCB 204 recovery F1	0.953	1.009	0.816	0.857	0.764
	$^{13}C_6$ δ-HCH BGB-172 F2	0.000	0.812	0.543	0.619	0.725
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.838	0.709	0.544	0.623	0.621
α-HCH	Measured Conc (ng)	ND	ND	ND	0.985	ND
	Wet wt (ng/g)	ND	ND	ND	0.051	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	9.93	ND
	EF	N/A	N/A	N/A	0.495	N/A
γ-HCH	Measured Conc (ng)	ND	ND	0.326	0.808	ND
	Wet wt (ng/g)	ND	ND	0.013	0.042	ND
	Lipid-normalized (ng/g lipid)	ND	ND	1.47	8.15	ND
	EF	N/A	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

Sample ID		660 NRPK	675 NRPK	NRPK 620	NRPK 815	NRPK 638
heptachlor	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	0.620	ND
	Wet wt (ng/g)	ND	ND	ND	0.032	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	6.24	ND
	EF	N/A	N/A	N/A	0.570	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	ND	0.255	1.21	ND
	Wet wt (ng/g)	ND	ND	0.010	0.063	ND
	Lipid-normalized (ng/g lipid)	ND	ND	1.15	12.2	ND
	EF	N/A	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

	Sample ID	660 NRPK	675 NRPK	NRPK 620	NRPK 815	NRPK 638
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	0.814	1.99	9.98	1.28	ND
	Wet wt (ng/g)	0.139	0.367	0.409	0.066	0.004
	Lipid-normalized (ng/g lipid)	24.8	46.9	44.9	12.9	0.472
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

5.12 Northern pike liver

	Species	NRPK LIVER	NRPK LIVER	NRPK LIVER	NRPK LIVER	NRPK LIVER
	Sample ID	NRPK615L	(742) NRPK C LIVER	660 NRPK LIVER	675 NRPK LIVER	NRPK573L
	Date Extracted	10/19/2005	3/24/2006	5/15/2006	5/15/2006	5/19/2006
	Fork Length (mm)	615	742	660	675	573
	Mass Extracted	3.363	10.682	6.678	5.062	6.529
	% Lipid	8.80	12.2	6.44	7.72	15.9
	Mass Lipid	0.296	1.30	0.430	0.391	1.04
	PCB 30 recovery F1	0.651	0.702	0.563	0.504	0.910
	PCB 204 recovery F1	N/A	0.882	0.984	0.967	1.14
	$^{13}C_6$ δ-HCH BGB-172 F2	0.476	N/A	0.764	0.660	0.672
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.457	N/A	0.787	0.720	0.672
α-HCH	Measured Conc (ng)	ND	N/A	24.9	21.9	31.1
	Wet wt (ng/g)	0.002	N/A	3.73	4.33	4.77
	Lipid-normalized (ng/g lipid)	0.022	N/A	57.9	56.0	29.9
	EF	N/A	N/A	0.559	0.508	0.565
γ-HCH	Measured Conc (ng)	ND	N/A	15.3	21.8	57.9
	Wet wt (ng/g)	0.002	N/A	2.30	4.30	8.86
	Lipid-normalized (ng/g lipid)	0.022	N/A	35.6	55.6	55.7
	EF	N/A	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	N/A	ND	ND	ND
	Wet wt (ng/g)	ND	N/A	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	N/A	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

Sample ID		NRPK615L	(742) NRPK C LIVER	660 NRPK LIVER	675 NRPK LIVER	NRPK573L
heptachlor	Measured Conc (ng)	ND	N/A	ND	ND	ND
	Wet wt (ng/g)	ND	N/A	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	N/A	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	N/A	ND	ND	ND
	Wet wt (ng/g)	ND	N/A	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	N/A	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	4.09	N/A	ND	1.79	2.56
	Wet wt (ng/g)	1.22	N/A	ND	0.353	0.392
	Lipid-normalized (ng/g lipid)	13.8	N/A	ND	4.57	2.46
	EF	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	N/A	ND	ND	ND
	Wet wt (ng/g)	ND	N/A	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	N/A	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	1.06	N/A	ND	0.943	0.775
	Wet wt (ng/g)	0.316	N/A	0.000	0.186	0.119
	Lipid-normalized (ng/g lipid)	3.59	N/A	0.004	2.41	0.745
	EF	N/A	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	N/A	ND	ND	ND
	Wet wt (ng/g)	ND	N/A	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	N/A	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	N/A	ND	ND	ND
	Wet wt (ng/g)	ND	N/A	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	N/A	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

	Sample ID	NRPK615L	(742) NRPK C LIVER	660 NRPK LIVER	675 NRPK LIVER	NRPK573L
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	61.0	242	26.0	40.8	97.6
	Wet wt (ng/g)	18.1	22.6	3.89	8.05	14.9
	Lipid-normalized (ng/g lipid)	206	185	60.4	104	93.9
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

5.13 Northern pike liver

	Species	NRPK LIVER	NRPK LIVER	NRPK LIVER	NRPK LIVER	NRPK LIVER
	Sample ID	NRPK580L	NRPK620L	NRPK620L2	NRPK815L	NRPK638L
	Date Extracted	5/19/2006	5/19/2006	7/10/2006	7/10/2006	8/3/2006
	Fork Length (mm)	580	620	620	815	638
	Mass Extracted	8.497	7.630	12.383	8.914	5.003
	% Lipid	11.31	7.62	9.43	8.07	6.16
	Mass Lipid	0.961	0.581	1.167	0.720	0.308
	PCB 30 recovery F1	0.637	2.39	0.266	0.094	0.280
	PCB 204 recovery F1	1.08	0.909	1.01	0.768	0.679
	$^{13}C_6$ δ-HCH BGB-172 F2	0.738	0.771	0.445	0.637	0.575
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.669	0.622	0.398	0.694	0.573
α-HCH	Measured Conc (ng)	17.0	9.74	2.21	ND	0.217
	Wet wt (ng/g)	2.00	1.28	0.179	ND	0.043
	Lipid-normalized (ng/g lipid)	17.7	16.7	1.89	ND	0.704
	EF	0.612	0.667	0.477	N/A	0.519
γ-HCH	Measured Conc (ng)	22.7	15.6	1.35	ND	0.160
	Wet wt (ng/g)	2.67	2.04	0.109	0.001	0.032
	Lipid-normalized (ng/g lipid)	23.6	26.8	1.15	0.009	0.519
	EF	N/A	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

Sample ID		NRPK580L	NRPK620L	NRPK620L2	NRPK815L	NRPK638L
heptachlor	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	1.19	ND	ND
	Wet wt (ng/g)	ND	ND	0.096	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	1.02	ND	ND
	EF	N/A	N/A	0.567	N/A	N/A
trans-nonachlor	Measured Conc (ng)	4.39	2.47	ND	ND	0.695
	Wet wt (ng/g)	0.517	0.324	0.001	0.001	0.139
	Lipid-normalized (ng/g lipid)	4.57	4.26	0.011	0.019	2.25
	EF	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF			N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	1.29	0.799	2.06	0.091	0.231
	Wet wt (ng/g)	0.152	0.105	0.166	0.010	0.046
	Lipid-normalized (ng/g lipid)	1.34	1.38	1.76	0.126	0.749
	EF	N/A	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	5.03	ND	ND
	Wet wt (ng/g)	ND	ND	0.406	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	4.31	ND	ND
	EF	N/A	N/A	0.465	N/A	N/A

Sample ID		NRPK580L	NRPK620L	NRPK620L2	NRPK815L	NRPK638L
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	163	451	37.4	110	21.2
	Wet wt (ng/g)	19.2	59.1	3.02	12.385	4.23
	Lipid-normalized (ng/g lipid)	170	775	32.0	153	68.6
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

5.14 Snail and spottail shiner

	Species	SNAIL	SPSH	SPSH	SPSH
	Sample ID	TBSN	WBSPSH	WBSPSH2	SPSH
	Date Extracted	7/7/2005	7/7/2005	7/7/2005	8/14/2006
	Fork Length (mm)	composite	minnow	minnow	composite
	Mass Extracted	10.2618	10.3969	9.5313	12.546
	% Lipid	0.58	2.85	1.67	1.26
	Mass Lipid	0.059	0.296	0.159	0.159
	PCB 30 recovery F1	0.422	0.573	0.189	0.241
	PCB 204 recovery F1	1.11	0.993	0.994	1.21
	$^{13}C_6$ δ-HCH BGB-172 F2	1.00	N/A	N/A	0.688
	$^{13}C_6$ δ-HCH β-Dex 120 F2	1.00	N/A	N/A	0.604
α-HCH	Measured Conc (ng)	ND	0.464	ND	ND
	Wet wt (ng/g)	ND	0.045	ND	ND
	Lipid-normalized (ng/g lipid)	ND	1.57	ND	ND
	EF	N/A	0.451	N/A	N/A
γ-HCH	Measured Conc (ng)	ND	0.928	2.33	1.05
	Wet wt (ng/g)	ND	0.089	0.244	0.084
	Lipid-normalized (ng/g lipid)	ND	3.14	14.6	6.61
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	TBSN	WBSPSH	WBSPSH2	SPSH
heptachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	0.191	ND	0.094
	Wet wt (ng/g)	ND	0.018	ND	0.007
	Lipid-normalized (ng/g lipid)	ND	0.647	ND	0.593
	EF	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	TBSN	WBSPSH	WBSPSH2	SPSH
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	1.30	6.46	3.38	6.96
	Wet wt (ng/g)	0.126	0.622	0.354	0.555
	Lipid-normalized (ng/g lipid)	21.9	21.8	21.2	43.9
	EF	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.15 Walleye and walleye liver

	Species	WALL	WALL	WALL LIVER	WALL LIVER
	Sample ID	WALL485-2	WALL540	WALL485-2	WALL 540
	Date Extracted	7/18/2006	7/27/2006	7/18/2006	7/27/2006
	Fork Length (mm)	485	540	485	540
	Mass Extracted	7.135	6.015	7.687	5.014
	% Lipid	1.19	0.84	5.14	8.33
	Mass Lipid	0.085	0.050	0.395	0.418
	PCB 30 recovery F1	0.719	N/A	N/A	0.532
	PCB 204 recovery F1	0.847	1.203	0.960	0.824
	$^{13}C_6$ δ-HCH BGB-172 F2	0.572	N/A	0.533	0.689
	$^{13}C_6$ δ-HCH β-Dex 120 F2	1.39	N/A	1.10	0.800
α-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
γ-HCH	Measured Conc (ng)	0.240	0.183	0.128	0.316
	Wet wt (ng/g)	0.034	0.030	0.017	0.063
	Lipid-normalized (ng/g lipid)	2.83	3.63	0.324	0.757
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	WALL485-2	WALL540	WALL485-2	WALL 540
heptachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	0.286	ND	0.103	0.203
	Wet wt (ng/g)	0.040	ND	0.013	0.041
	Lipid-normalized (ng/g lipid)	3.38	ND	0.260	0.487
	EF	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	0.336	ND
	Wet wt (ng/g)	ND	ND	0.044	ND
	Lipid-normalized (ng/g lipid)	ND	ND	0.850	ND
	EF	N/A	N/A	0.507	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	0.314	ND
	Wet wt (ng/g)	ND	ND	0.041	ND
	Lipid-normalized (ng/g lipid)	ND	ND	0.793	ND
	EF	N/A	N/A	0.484	N/A

	Sample ID	WALL485-2	WALL540	WALL485-2	WALL 540
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	ND	ND	ND	12.8
	Wet wt (ng/g)	ND	ND	ND	2.56
	Lipid-normalized (ng/g lipid)	ND	ND	ND	30.7
	EF	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.16 Whitesucker and yellow perch

	Species	WHSC	WHSC LIVER 5/19/06	YLPR	YLPR	YLPR
	Sample ID	WHSC060519	460 WHSC Liver (TB)	EBYLPR	WBYLPR	215 WBYLPR
	Date Extracted	10/1/2006	5/19/2006	7/7/2005	7/7/2005	7/29/2005
	Fork Length (mm)	450	460	2 fish	2 fish	204
	Mass Extracted	15.680	12.368	12.591	17.066	9.975
	% Lipid	3.75	7.28	2.73	2.61	5.19
	Mass Lipid	0.588	0.900	0.344	0.446	0.518
	PCB 30 recovery F1	N/A	0.187	0.444	0.486	N/A
	PCB 204 recovery F1	0.919	N/A	1.01	0.887	0.942
	$^{13}C_6$ δ-HCH BGB-172 F2	N/A	0.707	N/A	N/A	N/A
	$^{13}C_6$ δ-HCH β-Dex 120 F2	N/A	0.657	N/A	N/A	N/A
α-HCH	Measured Conc (ng)	ND	13.1	0.256	ND	ND
	Wet wt (ng/g)	ND	1.06	0.020	ND	ND
	Lipid-normalized (ng/g lipid)	ND	14.6	0.744	ND	ND
	EF	N/A	0.495	0.475	N/A	N/A
γ-HCH	Measured Conc (ng)	ND	45.8	0.654	ND	0.203
	Wet wt (ng/g)	ND	3.71	0.052	ND	0.020
	Lipid-normalized (ng/g lipid)	ND	50.9	1.90	ND	0.392
	EF	N/A	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

Sample ID		WHSC060519	460 WHSC Liver (TB)	EBYLPR	WBYLPR	215 WBYLPR
heptachlor	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	1.23	0.363
	Wet wt (ng/g)	ND	ND	ND	0.072	0.036
	Lipid-normalized (ng/g lipid)	ND	ND	ND	2.77	0.701
	EF	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	ND	ND	ND	0.188	0.067
	Wet wt (ng/g)	ND	ND	ND	0.011	0.007
	Lipid-normalized (ng/g lipid)	ND	ND	ND	0.421	0.130
	EF	N/A	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

	Sample ID	WHSC060519	460 WHSC Liver (TB)	EBYLPR	WBYLPR	215 WBYLPR
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	ND	12.6	9.88	7.65	ND
	Wet wt (ng/g)	ND	1.02	0.785	0.448	0.002
	Lipid-normalized (ng/g lipid)	ND	14.0	28.7	17.2	0.038
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

5.17 Yellow perch

	Species	YLPR	YLPR	YLPR	YLPR	YLPR
	Sample ID	YLPRTB	YLPREB	YLPRWB	YLPRTBMAY	YLPR WB
	Date Extracted	8/7/2006	8/7/2006	8/7/2006	8/7/2006	8/14/2006
	Fork Length (mm)	20 fish	20 fish	30 fish	11 fish	composite
	Mass Extracted	10.765	9.458	9.876	10.409	14.084
	% Lipid	2.51	3.43	2.55	1.68	1.51
	Mass Lipid	0.271	0.325	0.252	0.175	0.213
	PCB 30 recovery F1	0.107	1.09	0.381	0.442	0.269
	PCB 204 recovery F1	1.30	1.113	1.17	1.30	0.960
	$^{13}C_6$ δ-HCH BGB-172 F2	0.719	0.762	0.762	0.757	0.760
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.764	0.625	0.677	0.686	0.624
α-HCH	Measured Conc (ng)	ND	ND	ND	ND	0.327
	Wet wt (ng/g)	ND	ND	ND	ND	0.023
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	1.54
	EF	N/A	N/A	N/A	N/A	0.478
γ-HCH	Measured Conc (ng)	ND	ND	ND	ND	0.252
	Wet wt (ng/g)	0.001	0.001	0.001	0.001	0.018
	Lipid-normalized (ng/g lipid)	0.024	0.020	0.026	0.038	1.18
	EF	N/A	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

Sample ID		YLPRTB	YLPREB	YLPRWB	YLPRTBMAY	YLPR WB
heptachlor	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	0.669	0.642	0.526	0.524	ND
	Wet wt (ng/g)	0.062	0.068	0.053	0.050	0.001
	Lipid-normalized (ng/g lipid)	2.47	1.98	2.09	2.99	0.062
	EF	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	0.176	0.182	0.170	0.150	0.378
	Wet wt (ng/g)	0.016	0.019	0.017	0.014	0.027
	Lipid-normalized (ng/g lipid)	0.650	0.559	0.676	0.858	1.77
	EF	N/A	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

	Sample ID	YLPRTB	YLPREB	YLPRWB	YLPRTBMAY	YLPR WB
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	ND	23.8	0.335	2.72	6.04
	Wet wt (ng/g)	0.002	2.51	0.034	0.262	0.429
	Lipid-normalized (ng/g lipid)	0.072	73.1	1.33	15.5	28.4
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A

5.18 Yellow perch and yellow perch liver

	Species	YLPR	YLPR	YLPR LIV	YLPRLIV
	Sample ID	YLPR EB A	YLPR EB B	204 YLPRLIV	YLPRLIV COMPOSITE
	Date Extracted	8/14/2006	8/14/2006	7/29/2005	8/3/2006
	Fork Length (mm)	composite	composite	204	4 Liver
	Mass Extracted	13.077	12.487	1.309	2.952
	% Lipid	2.93	2.89	5.47	3.93
	Mass Lipid	0.383	0.361	0.072	0.116
	PCB 30 recovery F1	0.279	0.253	N/A	0.249
	PCB 204 recovery F1	0.986	0.963	0.851	1.71
	$^{13}C_6$ δ-HCH BGB-172 F2	0.666	0.768	N/A	0.652
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.513	0.616	N/A	0.593
α-HCH	Measured Conc (ng)	0.286	0.222	ND	ND
	Wet wt (ng/g)	0.022	0.018	ND	ND
	Lipid-normalized (ng/g lipid)	0.747	0.615	ND	ND
	EF	0.456	0.458	N/A	N/A
γ-HCH	Measured Conc (ng)	0.250	0.225	ND	0.142
	Wet wt (ng/g)	0.019	0.018	ND	0.048
	Lipid-normalized (ng/g lipid)	0.653	0.623	ND	1.22
	EF	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	YLPR EB A	YLPR EB B	204 YLPRLIV	YLPRLIV COMPOSITE
heptachlor	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	0.250
	Wet wt (ng/g)	0.001	0.001	ND	0.085
	Lipid-normalized (ng/g lipid)	0.035	0.037	ND	2.15
	EF	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	0.353	0.304	ND	0.086
	Wet wt (ng/g)	0.027	0.024	ND	0.029
	Lipid-normalized (ng/g lipid)	0.923	0.841	ND	0.743
	EF	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
cis-chlordane	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

	Sample ID	YLPR EB A	YLPR EB B	204 YLPRLIV	YLPRLIV COMPOSITE
p,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	8.57	7.42	ND	ND
	Wet wt (ng/g)	0.655	0.594	ND	ND
	Lipid-normalized (ng/g lipid)	22.4	20.5	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A

5.19 Certified Reference Material

	Species	1946A	EC-5	EC-5	EC-5	EC-5	EC-5
	Sample ID	060208 1946A	060614 EC-5	060515 EC-5	051019 EC-5	060718 EC-5	060807 EC-5
	Date Extracted	2/8/2006	6/14/06	06/11/06	10/19/05	7/18/06	8/7/06
	Fork Length (mm)						
	Mass Extracted	1.189	2.548	1.918	1.065	2.502	2.573
	% Lipid	21.88	0.00	0.00	0.00	0.00	0.00
	Mass Lipid	0.260	0.000	0.000	0.000	0.000	0.000
	PCB 30 recovery F1	0.245	0.568	0.281	0.575	0.616	N/A
	PCB 204 recovery F1	N/A	N/A	N/A	N/A	N/A	N/A
	$^{13}C_6$ δ-HCH BGB-172 F2	0.613	N/A	N/A	N/A	0.793	N/A
	$^{13}C_6$ δ-HCH β-Dex 120 F2	0.732	1.43	0.813	0.516	1.60	0.803
α-HCH	Measured Conc (ng)	1250	ND	0.175	ND	0.248	0.259
	Wet wt (ng/g)	1051	ND	0.091	ND	0.099	0.101
	Lipid-normalized (ng/g lipid)	4806	ND	ND	ND	ND	ND
	EF	0	N/A	0.344	N/A	0.357	0.306
γ-HCH	Measured Conc (ng)	173	ND	10.2	ND	0.224	0.236
	Wet wt (ng/g)	146	ND	5.31	ND	0.089	0.092
	Lipid-normalized (ng/g lipid)	666	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
β-HCH	Measured Conc (ng)	ND	ND	ND	ND	ND	0.316
	Wet wt (ng/g)	ND	ND	ND	ND	ND	0.123
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A

Sample ID		060208 1946A	060614 EC-5	060515 EC-5	051019 EC-5	060718 EC-5	060807 EC-5
heptachlor	Measured Conc (ng)	ND	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
oxychlordane	Measured Conc (ng)	27.6	ND	ND	ND	ND	ND
	Wet wt (ng/g)	23.2	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	106	ND	ND	ND	ND	ND
	EF	1	N/A	N/A	N/A	N/A	N/A
trans-nonachlor	Measured Conc (ng)	ND	ND	ND	ND	ND	7.94
	Wet wt (ng/g)	ND	ND	ND	ND	ND	3.08
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
heptachlor-*exo*-epoxide	Measured Conc (ng)	ND	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
cis-nonachlor	Measured Conc (ng)	111	ND	ND	ND	1.59	1.97
	Wet wt (ng/g)	93.3	ND	ND	ND	0.635	0.767
	Lipid-normalized (ng/g lipid)	427	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
trans-chlordane	Measured Conc (ng)	1.75E+03	6.84	6.24	6.40	8.09	10.7
	Wet wt (ng/g)	1.47E+03	2.68	3.25	6.01	3.23	4.14
	Lipid-normalized (ng/g lipid)	6.74E+03	ND	ND	ND	ND	ND
	EF	1	0.499	0.500	0.499	0.501	0.503
cis-chlordane	Measured Conc (ng)	6.61E+03	5.38	4.86	5.10	6.40	8.58
	Wet wt (ng/g)	5.56E+03	2.11	2.53	4.79	2.56	3.33
	Lipid-normalized (ng/g lipid)	2.54E+04	ND	ND	ND	ND	ND
	EF	0	0.498	0.497	0.504	0.496	0.502

	Sample ID	060208 1946A	060614 EC-5	060515 EC-5	051019 EC-5	060718 EC-5	060807 EC-5
p,p'-DDT	Measured Conc (ng)	317	ND	ND	ND	ND	ND
	Wet wt (ng/g)	267	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	1.22E+03	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
p,p'-DDE	Measured Conc (ng)	982	29.6	24.5	13.7	0.722	ND
	Wet wt (ng/g)	827	11.6	12.8	12.9	0.289	ND
	Lipid-normalized (ng/g lipid)	3.78E+03	N/A	N/A	N/A	N/A	N/A
	EF	N/A	N/A	N/A	N/A	N/A	N/A
o,p'-DDT	Measured Conc (ng)	ND	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
o,p'-DDD	Measured Conc (ng)	ND	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	N/A	N/A	N/A	N/A	N/A	N/A
o,p'-DDE	Measured Conc (ng)	ND	ND	ND	ND	ND	ND
	Wet wt (ng/g)	ND	ND	ND	ND	ND	ND
	Lipid-normalized (ng/g lipid)	ND	ND	ND	ND	ND	ND
	EF	ND	ND	ND	ND	ND	ND

6 Appendix II

Data analysis results as well as tables used to calculate values referred to in the body of the thesis are contained herein.

6.1 Unpaired *t*-test of NRPK fillet and NRPK liver

Parameter	Value
Table Analyzed:	
alpha-HCH	
Column J	NRPK
vs	vs
Column K	NRPK LIVER
Unpaired t test	
P value	0.0011
P value summary	**
Are means signif. different? (P < 0.05)	Yes
One- or two-tailed P value?	Two-tailed
t, df t=4.281 df=12	
How big is the difference?	
Mean ± SEM of column J	0.4317 ± 0.01635 N=7
Mean ± SEM of column K	0.5582 ± 0.02461 N=7
Difference between means	-0.1265 ± 0.02955
95% confidence interval	-0.1909 to -0.06211
R squared	0.6043
F test to compare variances	
F,DFn, Dfd	2.267, 6, 6
P value	0.1713
P value summary	ns
Are variances significantly different?	No

6.2 One-way ANOVA of oxychlordane in DCCO samples

Parameter	Value
Table Analyzed:	
all species	
oxychlordane concentrations ww	
One-way analysis of variance	
P value	P<0.0001
P value summary	***
Are means signif. different? (P < 0.05)	Yes
Number of groups	4
F	23.18
R squared	0.8634

ANOVA Table	SS	df	MS
Treatment (between columns)	62.50	3	20.83
Residual (within columns)	9.887	11	0.8988
Total	72.39	14	

Tukey's Multiple Comparison Test	Mean Diff.	q	P value	95% CI of diff
DCCO vs DCCO Chick liver	0.9076	1.915	P > 0.05	-1.110 to 2.925
DCCO vs DCCO Egg	-4.683	9.147	P < 0.001	-6.862 to -2.504
DCCO vs DCCO liver	0.1098	0.2317	P > 0.05	-1.908 to 2.127
DCCO Chick liver vs DCCO Egg	-5.591	10.92	P < 0.001	-7.770 to -3.412
DCCO Chick lvr vs DCCO lvr	-0.7978	1.683	P > 0.05	-2.815 to 1.220
DCCO Egg vs DCCO liver	4.793	9.362	P < 0.001	2.614 to 6.972

6.3 Two-tailed *t*-test of temperatures between Artland, SK 1983 and Lac La Biche, AB 2004

Parameter	Value
Table Analyzed	Artland 1983 and Lac La Biche 2004
Column A	Artland, SK 1983
vs	vs
Column B	Lac La Biche, AB 2004
Unpaired t test	
P value	0.6380
P value summary	ns
Are means signif. different? (P < 0.05)	No
One- or two-tailed P value?	Two-tailed
t, df t=0.4708 df=411	
How big is the difference?	
Mean ± SEM of column A	9.011 ± 0.6343 N=199
Mean ± SEM of column B	8.624 ± 0.5302 N=214
Difference between means	0.3872 ± 0.8224
95% confidence interval	-1.225 to 1.999
R squared	0.0005391
F test to compare variances	
F,DFn, Dfd	1.331, 198, 213
P value	0.0203
P value summary	*
Are variances significantly different?	Yes

6.4 Determination of Racemic values for OCs from standards

6.4.1 α-HCH

Number of values	58
Minimum	0.4600
25% Percentile	0.4948
Median	0.4992
75% Percentile	0.5034
Maximum	0.5198
Mean	0.4982
Std. Deviation	0.01074
Std. Error	0.001411
Lower 95% CI of mean	0.4954
Upper 95% CI of mean	0.5011
Normality Test	
KS distance	0.1504
P value	P > 0.10
Passed normality test (alpha=0.05)?	Yes
P value summary ns	
One sample t test	
Theoretical mean	0.5000
Actual mean	0.4982
Discrepancy	0.001755
95% CI of discrepancy	-0.004580 to 0.001071
t, df t=1.244 df=57	
P value (two tailed)	0.2186
Significant (alpha=0.05)?	No
Sum	28.90

6.4.2 *trans*-chlordane and *cis*-chlordane

	TC	CC
Number of values	55	54
Minimum	0.4476	0.4340
25% Percentile	0.4985	0.4950
Median	0.5013	0.5006
75% Percentile	0.5040	0.5085
Maximum	0.5106	0.5310
Mean	0.4991	0.5011
Std. Deviation	0.01049	0.01410
Std. Error	0.001414	0.001919
Lower 95% CI of mean	0.4963	0.4972
Upper 95% CI of mean	0.5020	0.5049
Normality Test		
KS distance	0.2542	0.1932
P value	0.0016	0.0355
Passed normality test (alpha=0.05)?	No	No
P value summary	**	*
One sample t test		
Theoretical mean	0.5000	0.5000
Actual mean	0.4991	0.5011
Discrepancy	0.0008701	-0.001078
95% CI of discrepancy	-0.003707 to 0.001967	-0.002773 to 0.004929
t, df	t=0.6154 df=54	t=0.5619 df=53
P value (two tailed)	0.5409	0.5765
Significant (α=0.05)?	No	No
Geometric mean	0.4990	0.5009
Lower 95% CI of geo. mean	0.4961	0.4969
Upper 95% CI of geo. mean	0.5020	0.5049
Sum	27.45	27.06

6.4.3 heptachlor-*exo*-epoxide

Number of values	14
Minimum	0.4781
25% Percentile	0.4910
Median	0.5009
75% Percentile	0.5125
Maximum	0.5410
Mean	0.5034
Std. Deviation	0.01700
Std. Error	0.004544
Lower 95% CI of mean	0.4936
Upper 95% CI of mean	0.5132
Normality Test	
KS distance	0.1785
P value	P > 0.10
Passed normality	Yes
P value summary	ns
One sample t test	
Theoretical mean	0.5000
Actual mean	0.5034
Discrepancy	-0.003387
95% CI of discrepancy	-0.006429 to 0.01320
t, df t=0.7453 df=13	
P value (two tailed)	0.4693
Significant (α=0.05)?	No
Geometric mean 0.5031	
Lower 95% CI of geo. mean	0.4935
Upper 95% CI of geo. mean	0.5129
Sum	7.047

6.4.4 oxychlordane

Number of values	40
Minimum	0.4513
25% Percentile	0.4983
Median	0.5012
75% Percentile	0.5046
Maximum	0.5510
Mean	0.5026
Std. Deviation	0.01581
Std. Error	0.002500
Lower 95% CI of mean	0.4976
Upper 95% CI of mean	0.5077
Normality Test	
KS distance	0.2583
P value	0.0096
Passed normality test (α=0.05)?	No
P value summary	**
One sample t test	
Theoretical mean	0.5000
Actual mean	0.5026
Discrepancy	-0.002628
95% CI of discrepancy	-0.002429 to 0.007685
t, df t=1.051 df=39	
P value (two tailed)	0.2995
Significant (α=0.05)?	No
Geometric mean 0.5024	
Lower 95% CI of geo. mean	0.4974
Upper 95% CI of geo. mean	0.5074
Sum	20.11

6.5 One-way ANOVA, Tukey's multiple comparison test of δ^{13}C in the Lac La Biche food web

Parameter	Value
Table Analyzed	
d13C	
One-way analysis of variance	
P value	P<0.0001
P value summary	***
Are means signif. different? (P < 0.05)	Yes
Number of groups	12
F	11.90
R squared	0.4440

ANOVA Table	SS	df	MS
Treatment (between columns)	136.5	11	12.41
Residual (within columns)	171.0	164	1.043
Total	307.5	175	

Tukey's Multiple Comparison Test	Mean Diff.	q	P value	95% CI of diff
CISC vs DCCO	-0.9378	2.755	P > 0.05	-2.542 to 0.6662
CISC vs Chick Breast	-0.5849	1.868	P > 0.05	-2.060 to 0.8906
CISC vs Chick Liver	-0.006334	0.01909	P > 0.05	-1.570 to 1.557
CISC vs LKWH	-1.358	3.131	P > 0.05	-3.403 to 0.6864
CISC vs NRPK	-1.478	3.407	P > 0.05	-3.523 to 0.5664
CISC vs SPSH	-0.7523	2.439	P > 0.05	-2.206 to 0.7014
CISC vs WALL	-1.493	3.924	P > 0.05	-3.287 to 0.2999
CISC vs WHSC	-1.427	4.193	P > 0.05	-3.031 to 0.1769
CISC vs YLPR	-0.09172	0.3399	P > 0.05	-1.363 to 1.180
CISC vs Snail	0.1416	0.5263	P > 0.05	-1.126 to 1.410
CISC vs Clam	1.594	5.737	P < 0.01	0.2848 to 2.904
DCCO vs Chick Breast	0.3529	1.127	P > 0.05	-1.123 to 1.828
DCCO vs Chick Liver	0.9314	2.808	P > 0.05	-0.6319 to 2.495
DCCO vs LKWH	-0.4206	0.9693	P > 0.05	-2.465 to 1.624
DCCO vs NRPK	-0.5406	1.246	P > 0.05	-2.585 to 1.504
DCCO vs SPSH	0.1855	0.6012	P > 0.05	-1.268 to 1.639
DCCO vs WALL	-0.5556	1.460	P > 0.05	-2.349 to 1.238
DCCO vs WHSC	-0.4893	1.438	P > 0.05	-2.093 to 1.115
DCCO vs YLPR	0.8461	3.135	P > 0.05	-0.4256 to 2.118
DCCO vs Snail	1.079	4.011	P > 0.05	-0.1887 to 2.347
DCCO vs Clam	2.532	9.112	P < 0.001	1.223 to 3.842
Chk Brst vs Chk Lvr	0.5785	1.905	P > 0.05	-0.8527 to 2.010
Chk Brst vs LKWH	-0.7735	1.874	P > 0.05	-2.719 to 1.172
Chick Breast vs NRPK	-0.8935	2.164	P > 0.05	-2.839 to 1.052
Chick Breast vs SPSH	-0.1674	0.6021	P > 0.05	-1.478 to 1.143
Chick Breast vs WALL	-0.9085	2.549	P > 0.05	-2.588 to 0.7708
Chick Breast vs WHSC	-0.8422	2.690	P > 0.05	-2.318 to 0.6332
Chick Breast vs YLPR	0.4932	2.103	P > 0.05	-0.6120 to 1.598
Chick Breast vs Snail	0.7265	3.110	P > 0.05	-0.3745 to 1.827
Chick Breast vs Clam	2.179	8.941	P < 0.001	1.031 to 3.328
Chick Liver vs LKWH	-1.352	3.165	P > 0.05	-3.365 to 0.6610

Tukey's Multiple Comparison Test	Mean Diff.	q	P value	95% CI of diff
Chick Liver vs NRPK	-1.472	3.446	P > 0.05	-3.485 to 0.5410
Chick Liver vs SPSH	-0.7460	2.495	P > 0.05	-2.155 to 0.6628
Chick Liver vs WALL	-1.487	3.988	P > 0.05	-3.244 to 0.2700
Chick Liver vs WHSC	-1.421	4.283	P > 0.05	-2.984 to 0.1426
Chick Liver vs YLPR	-0.08538	0.3298	P > 0.05	-1.305 to 1.135
Chick Liver vs Snail	0.1480	0.5733	P > 0.05	-1.068 to 1.364
Chick Liver vs Clam	1.601	5.989	P < 0.01	0.3412 to 2.860
LKWH vs NRPK	-0.1200	0.2350	P > 0.05	-2.526 to 2.286
LKWH vs SPSH	0.6060	1.480	P > 0.05	-1.323 to 2.535
LKWH vs WALL	-0.1350	0.2897	P > 0.05	-2.331 to 2.061
LKWH vs WHSC	-0.06875	0.1585	P > 0.05	-2.113 to 1.976
LKWH vs YLPR	1.267	3.324	P > 0.05	-0.5293 to 3.062
LKWH vs Snail	1.500	3.942	P > 0.05	-0.2934 to 3.293
LKWH vs Clam	2.953	7.633	P < 0.001	1.130 to 4.776
NRPK vs SPSH	0.7260	1.774	P > 0.05	-1.203 to 2.655
NRPK vs WALL	-0.01504	0.03227	P > 0.05	-2.211 to 2.181
NRPK vs WHSC	0.05124	0.1181	P > 0.05	-1.993 to 2.096
NRPK vs YLPR	1.387	3.639	P > 0.05	-0.4093 to 3.182
NRPK vs Snail	1.620	4.257	P > 0.05	-0.1734 to 3.413
NRPK vs Clam	3.073	7.944	P < 0.001	1.250 to 4.896
SPSH vs WALL	-0.7411	2.103	P > 0.05	-2.401 to 0.9192
SPSH vs WHSC	-0.6748	2.187	P > 0.05	-2.129 to 0.7790
SPSH vs YLPR	0.6606	2.893	P > 0.05	-0.4154 to 1.737
SPSH vs Snail	0.8939	3.931	P > 0.05	-0.1778 to 1.966
SPSH vs Clam	2.347	9.869	P < 0.001	1.226 to 3.467
WALL vs WHSC	0.06628	0.1742	P > 0.05	-1.727 to 1.860
WALL vs YLPR	1.402	4.393	P > 0.05	-0.1018 to 2.905
WALL vs Snail	1.635	5.135	P < 0.05	0.1346 to 3.135
WALL vs Clam	3.088	9.476	P < 0.001	1.552 to 4.624
WHSC vs YLPR	1.335	4.949	P < 0.05	0.06368 to 2.607
WHSC vs Snail	1.569	5.830	P < 0.01	0.3007 to 2.837
WHSC vs Clam	3.022	10.87	P < 0.001	1.712 to 4.331
YLPR vs Snail	0.2333	1.361	P > 0.05	-0.5744 to 1.041
YLPR vs Clam	1.686	9.117	P < 0.001	0.8146 to 2.558
Snail vs Clam	1.453	7.904	P < 0.001	0.5866 to 2.319

6.6 One sample *t*-test of α-HCH EFs in NRPK and NRPK liver to that of racemic standard

	NRPK	NRPK LIVER
Number of values	7	7
Minimum	0.3772	0.4770
25% Percentile	0.3953	0.5084
Median	0.4404	0.5593
75% Percentile	0.4610	0.6122
Maximum	0.4955	0.6671
Mean	0.4317	0.5582
Std. Deviation	0.04326	0.06512
Std. Error	0.01635	0.02461
Lower 95% CI of mean	0.3917	0.4980
Upper 95% CI of mean	0.4717	0.6185
Normality Test		
KS distance	0.2256	0.1748
P value	P > 0.10	P > 0.10
Passed normality test (alpha=0.05)?	Yes	Yes
P value summary	ns	ns
One sample t test		
Theoretical mean	0.4982	0.4982
Actual mean	0.4317	0.5582
Discrepancy	0.06647	-0.06002
95% CI of discrepancy	-0.1065 to -0.02647	-0.0002104 to 0.1203
t, df	t=4.066 df=6	t=2.438 df=6
P value (two tailed)	0.0066	0.0506
Significant (alpha=0.05)?	Yes	No
Sum	3.022	3.908

6.7 Column statistics summary for % γ-HCH in samples from Lac La Biche

	Cisco	Cisco Liver	DCCO	DCCO Chick Liver	DCCO Egg	DCCO Liver	LKWH Liver
Number of values	3	4	2	1	3	1	2
Minimum	52.46	100.0	100.0	68.43	0.0	100.0	46.92
25% Percentile	100.0						
Median	100.0	100.0	100.0	68.43	32.39	100.0	62.94
75% Percentile	100.0						
Maximum	100.0	100.0	100.0	68.43	37.41	100.0	78.96
Mean	84.15	100.0	100.0	68.43	23.27	100.0	62.94
Std. Deviation	27.45	0.0	0.0	0.0	20.31	0.0	22.66
Std. Error	15.85	0.0	0.0	0.0	11.72	0.0	16.02
Lower 95% CI of mean	15.97	100.0	100.0	100.0	-27.18	-27.18	-140.6
Upper 95% CI of mean	152.3	100.0	100.0	100.0	73.71	73.71	266.5
Coefficient of variation	32.62%	0.00%	0.00%	0.00%	87.27%	0.00%	36.00%
Geometric mean	80.65	100.0	100.0	68.43		100.0	60.86
Lower 95% CI of geo. mean	31.97	100.0	100.0	0.0		0.0	2.229
Upper 95% CI of geo. mean	203.5	100.0	100.0	0.0		0.0	1662
Sum	252.5	400.0	200.0	68.43	69.80	100.0	125.9

	NRPK	NRPK Liver	SPSH	WALL	WALL Liver	WHSC Liver	YLPR
Number of values	2	8	3	2	2	1	5
Minimum	45.07	0.0	66.68	100.0	100.0	77.74	43.52
25% Percentile	37.98					45.09	
Median	72.54	46.15	100.0	100.0	100.0	77.74	50.31
75% Percentile	59.36					85.94	
Maximum	100.0	65.02	100.0	100.0	100.0	77.74	100.0
Mean	72.54	44.00	88.89	100.0	100.0	77.74	62.47
Std. Deviation	38.84	20.59	19.24	0.0	0.0	0.0	23.74
Std. Error	27.46	7.280	11.11	0.0	0.0	0.0	10.62
Lower 95% CI of mean	-276.4	26.78	41.11	100.0	100.0	100.0	33.00
Upper 95% CI of mean	421.5	61.22	136.7	100.0	100.0	100.0	91.95
Coefficient of variation	53.55%	46.80%	21.64%	0.00%	0.00%	0.00%	38.00%
Geometric mean	67.13		87.37	100.0	100.0	77.74	59.32
Lower 95% CI of geo. mean	0.4248		48.86	100.0	100.0	0.0	38.41
Upper 95% CI of geo. mean	10611		156.2	100.0	100.0	0.0	91.61
Sum	145.1	352.0	266.7	200.0	200.0	77.74	312.4

6.8 Isomeric composition determination of HCH in eggs of double-crested cormorants from the Great Lakes (Yamashita *et al.* 1993)

Isomer	%								average	stdev	geo met
alpha	26	27	32	28	33	35	30	27	30	3	30
beta	57	59	54	61	52	43	57	54	55	5	54
gamma	17	15	14	11	14	22	13	20	16	3	15

6.9 *p,p'*-DDE biomagnification factor between adult double-crested cormorants and yellow perch

$$\frac{1260\,ng/g_{lipid}}{18.04\,ng/g_{lipid}} = 69.84$$

6.10 Regression analysis of log lipid versus δ^{15}nitrogen plots

6.10.1 oxychlordane, *trans*-nonachlor, and *cis*-nonachlor

	oxychlordane	*trans*-nonachlor	*cis*-nonachlor
Best-fit values			
Slope	1.190 ± 0.01332	0.2703 ± 0.01685	0.2120 ± 0.2262
Y-intercept	-14.03 ± 0.1709	-2.261 ± 0.1853	-1.883 ± 2.684
X-intercept	11.79	8.363	8.882
1/slope	0.8406	3.699	4.716
95% Confidence Intervals			
Slope	1.020 to 1.359	0.05621 to 0.4844	-2.662 to 3.086
Y-intercept when X=0.0	-16.20 to -11.85	-4.615 to 0.09338	-35.99 to 32.22
X-intercept when Y=0.0	11.61 to 11.92	-1.623 to 9.752	to
Goodness of Fit			
r≤	0.9999	0.9961	0.4677
Sy.x	0.006197	0.03823	0.4411
Is slope significantly non-zero?			
F	7981	257.3	0.8786
DFn, DFd	1.000, 1.000	1.000, 1.000	1.000, 1.000
P value	0.0071	0.0396	0.5206
Deviation from zero?	Significant	Significant	Not Significant
Data			
Number of X values	3	3	3
Maximum number of Y replicates	1	1	1
Total number of values	3	3	3
Number of missing values	3	3	3

6.10.2 *p,p'*-DDE

	DCCO and YLPR	Fishes	Overall Food web
Best-fit values			
Slope	0.5122 ± 0.1827	0.09967 ± 0.03459	0.1959 ± 0.06648
Y-intercept	-3.171 ± 2.207	0.9149 ± 0.3558	0.2067 ± 0.7295
X-intercept	6.191	-9.180	-1.055
1/slope	1.952	10.03	5.105
95% Confidence Intervals			
Slope	-0.2738 to 1.298	0.01073 to 0.1886	0.04549 to 0.3463
Y-intercept when X=0.0	-12.67 to 6.325	0.0001169 to 1.830	-1.444 to 1.857
X-intercept when Y=0.0	9.899 to 22.77	-167.5 to -0.0006311	-40.04 to 4.250
Goodness of Fit			
r≤	0.7972	0.6241	0.4910
Sy.x	0.4175	0.2565	0.5632
Is slope significantly non-zero?			
F	7.862	8.302	8.680
DFn, DFd	1.000, 2.000	1.000, 5.000	1.000, 9.000
P value	0.1071	0.0345	0.0163
Deviation from zero?	Not Significant	Significant	Significant
Data			
Number of X values	4	7	11
Maximum number of Y replicates	1	1	1
Total number of values	4	7	11
Number of missing values	7	4	0